Tuning the properties of InAs/GaAs quantum dots through a modified capping layer

Application to optoelectronic devices

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through a modified capping layer: Application to
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ما بك لن يدم

Abstract

Quantum-dot (QD) technology has become a very transversal technology finding application in an increasing number of scientific and industrial fields. At the forefront of this development is the well-studied InAs/GaAs QD system. However, the limitations imposed by the fixed InAs-GaAs band offsets and by the difficulties to control the QD morphology due to the capping process still difficult the precise control of QD band structure that would allow the required design in different applications. The use of a certain capping layer (CL) material different than GaAs has been particularly employed to tune the ground state energy of InAs/GaAs QDs through strain and band structure engineering, so achieving the long-wavelength telecommunication windows as one of the most pursued targets. This work is mainly focused on the achievement of a higher tunability of the properties of InAs/GaAs QDs by the application of thin GaAs(Sb)(N) CLs and the optimization of the capping process in order to improve their suitability to any optoelectronic device, and more in particular to laser diodes and solar cells. GaAs(Sb)(N)/InAs/GaAs QDs are a highly versatile system in which the use of Sb and N allows for the tunability of the QD ground state while providing a huge degree of freedom regarding the QD-CL band-alignment, according to the requirements of the field of application.

As starting point, a very straightforward approach is shown to controllably tune the structural and optical properties of InAs/GaAs QDs without the need for strain-engineering strategies. The QD dissolution process, induced by the surface In-Ga intermixing taking place during overgrowth, is shown to be kinetically controlled by the mere adjust of the capping rate. This parameter allows not only for the control of the final structural properties of the QD and, therefore, of its optical properties, but also for the control of the wetting layer (WL) thickness, known to directly affect the performance of QD-based devices. This approach therefore represents an additional degree of freedom in the tunability of the QD properties, which can be combined with alternative approaches, such as the application of different CL materials.

The use of GaAsSb CLs is found to improve the characteristics of both QD lasers and solar cells. On one side, GaAsSb CLs are shown reduce the threshold current density of QD lasers while extending the lasing wavelength with the Sb content. This structure improves the external differential quantum efficiency in a type-I QD-CL band alignment configuration and provides the devices with a higher thermal stability in a type-II configuration. On the other side, GaAsSb CLs are shown to tune the absorption edge of QD solar cells, enhancing infrared photoresponse, while providing themselves strong additional photocurrent. Such a device acts therefore as a hybrid QD-quantum well solar cell. This, along with an improved carrier collection arising from the type-II WL-CL band alignment, yields improved conversion efficiencies, even for high Sb contents giving rise to the formation of extended defects.

This suggests the possibility to achieve improved performance in combination with strain-balancing techniques, such as the addition of N to the CL.

Despite the promising versatility of GaAsSbN CLs, an optimization of the growth process is required prior to their use in any QD-based device. The search for the optimum CL growth conditions reveals the great impact of the capping rate, improving significantly the growth of the quaternary GaAsSbN CLs on InAs/GaAs QDs, leading to the achievement of room-temperature emission. On the other hand, the idea of an ultrashort-period GaAsSb/GaAsN superlattice CL, leads to the achievement of further extended emission at room temperature and efficient LED emission, comparable to that of LEDs containing GaAsSb CLs, known to be very efficient.

The addition of N is shown to allow for the compensation of the accumulated strain in stacked QD structures for solar cells, not only in ternary GaAsN CLs, but also in quaternary GaAsSbN CLs, relieving the accumulated strain introduced by the presence of Sb. In addition, the use of N in the CL is found to extend the photoresponse of a QD solar cell, further extending it in combination with Sb through an independent control of the conduction and valence band confinement within the QD. However, although N-containing CLs provide an enhanced absorption, the presence of N induces electron trapping effects, worsening carrier collection efficiency. Alternative approaches are therefore proposed in order to improve the conversion efficiency. In particular, the CL potential depth, thickness, and structure, as well as the resulting band alignment, are found to play an important role in carrier extraction and transport in QD solar cells.

Resumen

La tecnología de punto cuántico (QD) se ha convertido en una tecnología muy transversal, encontrando aplicación en un número creciente de campos científicos e incluso industriales. Esto se debe en gran medida al desarrollo experimentado por los QDs auto-ensamblados de InAs/GaAs. Sin embargo, las limitaciones impuestas por los band offsets fijos entre InAs-GaAs y por las dificultades para controlar la morfología de los QDs (debido, en particular, al proceso de capping) todavía dificultan un control preciso de la estructura de bandas del punto que permitiría el diseño adecuado en diferentes aplicaciones. En particular, se han utilizado capas de recubrimiento (CLs) constituidas por un determinado material para ajustar la energía del estado fundamental de QDs de InAs/GaAs mediante la ingeniería de bandas y de deformación, alcanzando las longitudes de onda de las ventanas de transmisión en comunicaciones de fibra óptica, como uno de los objetivos más perseguidos. Este trabajo está principalmente enfocado en la obtención de una mayor capacidad de ajuste de las propiedades de los QDs de InAs/GaAs mediante la aplicación de CLs finos de GaAs(Sb)(N) y la optimización del proceso de recubrimiento, con el fin de mejorar su adecuación a un determinado dispositivo, y más en particular a diodos láser y células solares. Los QDs de GaAs(Sb)(N)/InAs/GaAs son un sistema muy versátil en el que el uso de Sb y N permite modificar la energía del nivel fundamental del punto a la vez que ofrece un alto grado de libertad con respecto al alineamiento de bandas en la estructura QD-CL, de acuerdo a las necesidades del campo de aplicación.

Como punto de partida, se propone un enfoque que permite controlar de forma directa las propiedades ópticas y estructuras del QD de InAs/GaAs sin la necesidad de recurrir a estrategias de ingeniería de deformación. El proceso de disolución del QD, inducido por el entremezclado entre átomos de In y Ga que tiene lugar durante el recubrimiento, es controlado cinéticamente por el simple ajuste de la velocidad de recubrimiento. Este parámetro hace posible no sólo controlar las propiedades estructurales finales del QD y, por lo tanto, sus propiedades ópticas, sino también el espesor de la capa de mojado (WL), cuyo impacto en el rendimiento de operación de dispositivos de QD puede ser muy relevante. Por lo tanto, este enfoque representa un grado de libertad adicional en la modificación de las propiedades de QD que puede aplicarse en combinación con enfoques alternativos, como el uso de CLs de diferentes materiales.

Se demuestra una mejora de las propiedades tanto de láseres como de células solares de QD con el uso de CLs de GaAsSb. Por un lado, la aplicación de CLs de GaAsSb reduce la densidad de corriente umbral de láseres de QD a la vez que extiende la longitud de onda de emisión láser al aumentar el contenido de Sb. Esta estructura mejora la eficiencia cuántica externa diferencial en una configuración de alineamiento de bandas de QD-CL tipo I y confiere a los dispositivos una mayor estabilidad térmica en una configuración de alineamiento de bandas de QD-CL tipo II. Por otro lado, el uso de CLs de GaAsSb permite ajustar el borde

de absorción de una célula solar de QD, mejorando la fotorespuesta en el infrarrojo. Además, el CL contribuye por sí mismo a aumentar la fotorespuesta con una significativa fotocorriente adicional. Tales dispositivos funcionan, por tanto, como células solares híbridas de QD-pozo cuántico. Esto, junto con una mejor colección de portadores debido al alineamiento tipo II en la estructura WL-CL, produce una mejora de la eficiencia de conversión, incluso para altos contenidos de Sb que dan lugar a la formación de defectos extensos. Esto sugiere la posibilidad de conseguir mayores rendimientos en combinación con técnicas de compensación de deformación, como por ejemplo la adición de N al CL.

A pesar de la prometedora versatilidad de los CLs de GaAsSbN, se requiere una optimización del proceso de crecimiento previa a su uso en cualquier dispositivo basado en QDs. La búsqueda de las condiciones óptimas de crecimiento del CL revela el gran impacto de la velocidad de recubrimiento: velocidades altas mejoran significativamente el crecimiento de los CLs cuaternarios de GaAsSbN sobre QDs de InAs/GaAs, permitiendo la obtención de emisión de fotoluminiscencia a temperatura ambiente. Por otro lado, la idea de un CL cuaternario con estructura de superred de periodo corto, constituida por la secuencia alterna de ambos ternarios GaAsSb y GaAsN, da lugar a la obtención de emisión a temperatura ambiente en longitudes de onda más largas y a una emisión LED eficiente, comparable a la de LEDs basados en puntos recubiertos con GaAsSb, de alta eficiencia.

Se demuestra una compensación de la deformación acumulada en estructuras de QD apiladas para células solares mediante la adición de N, no sólo en CL ternarios de GaAsN, sino también en CLs cuaternarios de GaAsSbN, relajando la deformación acumulada por la adición de Sb. Además, el uso de N en el CL lleva también a una extensión de la fotorespuesta de células solares de QD, mayor en combinación con Sb, por medio de un control independiente del confinamiento en la banda de conducción y de valencia en el QD. Sin embargo, aunque el uso de CLs con contenido en N da lugar a una mayor absorción, la presencia de N induce efectos de atrapamiento de electrones, empeorando la eficiencia de colección. Se requieren, por lo tanto, enfoques alternativos con el fin de mejorar la eficiencia de conversión. En particular, se demuestra que parámetros como la profundidad del pozo de potencial en el CL, su espesor, y su estructura, así como el alineamiento de bandas resultante, juegan un papel importante en la extracción y el transporte de portadores en células solares de QD.

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1 Introduction and Objectives

1.1. Motivation: State of the art

Be they in the form of diodes or transistors, semiconductors are essential in every aspect of our daily life. Semiconductor diodes find application in different optoelectronic devices such as light emitting diodes (LEDs), used in bulbs and display applications (display panels, televisions or mobile phones, among others), and laser diodes (LDs), which are fundamental in digital storage (CD, DVD, and blue-ray players), as well as in communication systems (optical fiber amplifiers and photodetectors). Nevertheless, the presence of semiconductors is not restricted to optoelectronic systems. While semiconductor diodes are also used in radio modulation/demodulation, power conversion (AC into DC), or logic gates as the basis of digital electronics, semiconductor transistors represent the foundation of integrated circuits, which are the origin of microprocessors and, therefore, of current computers. Semiconductors are ubiquitous in modern technology, being necessary not only for the operation of any home appliance or consumer electronics device, but also in industrial machines, medical instruments or even social infrastructures. Semiconductors are also the cornerstone of the progress in photovoltaic power supply, leading to breathtaking improvements in conversion efficiencies year after year and becoming indispensable for the preservation of the global environment. Semiconductors technology has in some cases replaced an older one giving rise to cheaper, faster, and more compact and reliable devices, while many other uncountable applications would be otherwise unimaginable. However, it has been a long way to get here along which a series of advances has been essential.

The history of semiconductors started to be written when Michel Faraday observed, in 1833, the effect that temperature exerts on the conductivity of such materials [1]. Soon afterwards, in 1839, Alexandre-Edmond Becquerel discovered the photovoltaic effect [2]. However, it was not until around one century later that such properties of semiconductors were attributed to their low energy band gap and the unavoidable and necessary presence of impurities. These particularities of semiconductors, together with the rectification in metal-semiconductor junctions, discovered in the late 19th century by Karl Ferdinand Braun, the inventor of the so called cat's whisker diode [3], provide the foundations for a field of science encompassing uncountable applications. It was in 1883, almost half a century after Becquerel's discovery, when the first solar cell would see the sunlight, made by Charles Fritts from a metal plate and a thin selenium layer covered with gold and whose efficiency was below 1% [4]. The reverse phenomenon, the emission of light originating from a driven current, was first reported by Henry Joseph Round in 1907 on a Schottky contact formed on SiC [5].

The invention of the bipolar transistor in 1947 (Bell Laboratories) [6], would represent the beginning of the semiconductor technology revolution, boosting the research on different

semiconductor materials. Ever since, ceaseless research on suitable materials for electronic devices was carried out, GaAs playing a main role. GaAs was considered a good candidate owing to its superior electron dynamics, expected to allow for the implementation of faster transistors for high-frequency applications. Although GaAs was initially conceived for bipolar junction transistors, faster achievements were obtained in field effect transistors (FETs), more specifically, in metal-semiconductor FETs. The real breakthrough came at the hand of the development of two new growth techniques: molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). Such techniques allowed for the practical realization of devices based on high-crystalline-quality heterostructures, fulfilling the requirements for high-frequency operation [7] and rocketing the operation frequency of GaAs-based bipolar transistors in the forthcoming years.

GaAs has also played a main role in the development of optoelectronic applications and devices. Since a direct gap is necessary for an efficient light emission capability, Si and Ge are not competitors in the least, so that laser action was first reported in 1962 using GaAs [8–10] and GaAsP [11] junctions. Moreover, compound semiconductors present the advantage that they can be alloyed, allowing a large tunability of the semiconductor band gap and the realization of the double heterostructure (DHS) as the active region of a semiconductor laser [12,13]. Such a structure was conceived as a means to confine electrons and holes inside the active region, enhancing population inversion by avoiding thermal carrier escape and improving homojunction laser performance. The first DHS laser was reported in 1967 using GaAsP [14]. However, $\text{GaAs}_{1-x}\text{P}_x$ is an incompatible-lattice system (see Fig. 1.1) and defects arise as the amount of P increases reducing the device efficiency, so that lasing occurred only at liquid-nitrogen temperatures. $\text{Al}_x\text{Ga}_{1-x}\text{As}$, however, was shortly afterwards found to be a lattice-matched system allowing for the achievement of higher emission energies and lasing at room temperature (RT) [15,16]. Since then, research efforts started to focus also on quaternary materials, which allow for an independent control of the band gap and the lattice constant.

The introduction of MBE and MOVPE growth techniques had a strong impact on the development of such materials, allowing for a high degree of control in the composition of ternary and quaternary compounds unreachable by the techniques commonly used until then. In addition, the precise dimensional control of the layer thickness to the atomic order allowed for the growth of active regions of the order of a few nanometers with abrupt interfaces and high crystalline quality. Such a structure, with a thickness lower than the de Broglie wavelength of the charge carrier, restricts the carrier motion in the out-plane direction, representing what today is called a quantum well (QW). Advantages with respect to bulk materials were expected from QWs, due to the quantum confinement of carriers, such as a higher gain, resulting in lower threshold current densities (J_{th}), and high wavelength adjustability by merely modifying the QW thickness. The first QW laser demonstration was on optically pumped devices grown by liquid phase epitaxy (LPE) in 1975 [17] taking only one more year to achieve lasing at RT [18], although with very high equivalent threshold injection

current densities. The early low thresholds found in DHS lasers grown by MOCVD [19], comparable to those achieved by LPE [20,21], motivated the growth of QW lasers through this growth method, demonstrating the first QW injection laser [22]. However, the advantages of QW lasers arrived with their development by MBE, progressively reducing thresholds [23–25], and further improving them by the introduction of more complicated active region structures [26]. The idea of combining strain and quantum confinement [27] also resulted in similar improvements using InGaAs QWs on GaAs substrates [28].

Fig. 1.1: Band gap energy versus lattice constant for III-V semiconductors as reported in [29].

However, lattice parameter mismatch between compound and host materials may lead to the relaxation of the structure and the origination of extended defects, representing a challenge for efficient emission. An excessive accumulation of strain due to lattice mismatch typically induces a three-dimensional growth mode, called the Stranski-Krastanow mechanism [30]. It was not until the 1990s when such islands were considered as a possible realization of quantum dots (QDs), showing three-dimensional carrier confinement. The MBE growth technique allowed not only for the realization of self-assembled QDs, but also without interface defects, making possible the implementation of the first QD laser, based on InGaAs/GaAs, in 1994 [31]. A reduction in the dimensionality of the active region and, therefore, the density of states, was expected to provide lasers with improved characteristics.

Furthermore, lower temperature-sensitive threshold currents had also been years before predicted for lower and lower semiconductor dimensionalities [32,33]. Over a few years, such properties of InGaAs QD lasers improved even exceeding predictions [34–37] (see Fig. 1.2).¹

Fig. 1.2: Progress on the threshold current density of semiconductor injection lasers based on DHS, QW and QD structures.

Although different QD systems have been researched for the last few years, none of them has shown better characteristics than the InAs/GaAs² system as yet. This makes this system

¹ It must be noted that the power achievable from a QD laser is much lower than that from a conventional DHS laser. Nevertheless, there are very interesting specific applications of QD lasers such as low energy consumption and high-speed data communication systems or mode-locked lasers for optical data storage. Indeed it has been argued that future interconnect technology will require micrometer size optical components in a chip consuming less than a femtojoule per bit [38].

² The notation used in this thesis to refer to the materials in a certain QD system is *QD/Substrate*. When highlighting the capping layer (CL) material, which may or not be different from that of the substrate, the notation *CL/QD/Substrate* will be followed.

a potential candidate for efficient emitting devices substituting the currently implemented InP-technology for the second and third fiber-optic telecommunication windows. Indeed, GaAs-based technology presents some advantages which have aroused great scientific and technological interest. On one side, the high refractive index contrast of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ lattice-matched system allows for the growth of efficient GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ distributed Bragg reflectors. On the other side, the higher conduction band offsets make devices based on GaAs present a lower carrier leakage than those based on InP, which are highly temperature sensitive. This would allow dispensing with the incorporation of cooling systems, what added to the much lower price of GaAs substrates makes this system more economically viable.

The intensive research on InAs/GaAs QDs has led to obtain emission over a wide range of wavelengths through different approaches, including telecommunication wavelengths [39–43]. Indeed, a QD laser at the 1.3 μm communication wavelength was soon developed [44] and nowadays there are some companies³ marketing InAs/GaAs QD lasers operating between 1064 nm and 1320 nm. However, lasing at 1.55 μm continues to be unreachable by this system, so that many efforts are nowadays focused on this aim. Moreover, novel approaches such as QD lasers with a type-II band alignment are still almost unexplored.

The impressive advances in LDs due to the implementation of QDs have not yet been reproduced in other fields which could also experiment revolutionary advances in the near future taking advantage of QD technology. Indeed, QDs have recently been considered as an also promising approach for photovoltaic applications. This was first motivated by the idea of absorbing additional light energies inside the gap material and increase the short-circuit current density (J_{sc}). Additional advantageous properties have also been attributed to QD solar cells. The so-called multiple-exciton generation (MEG) mechanism, carrier multiplication in QDs, has been theoretically predicted to be more efficient than in bulk materials [45]. In fact, MEG has already been reported in different QD systems [46–53]. Such a mechanism allows harnessing part of the excess kinetic energy of photogenerated carriers leading to the origination of additional carrier pairs, so that an enhanced photocurrent (PC) is achieved. QDs have also been proposed as a possibility to develop the intermediate-band solar cell concept [54], predicted to exceed the Shockley-Queisser efficiency limit for an ideal solar cell [55,56], focusing most attempts on the InAs/GaAs system [57–59]. Indeed, the necessary formation of three quasi-Fermi levels required by the intermediate-band solar-cell theory, describing the carrier population of the valence, intermediate, and conduction bands, has been demonstrated in a QD solar cell [58], as well as, albeit at low temperatures, QD-mediated PC from two-photon absorption [60]. However, despite the expectations, no QD solar cell has been shown to exceed the performance of an equivalent reference one yet.

³ See, for instance, Innolume GmbH, a company founded in 2003 that claims to be the premier manufacturer of QD-based LDs and modules, or QD Laser, Inc., a subsidiary of Fujitsu Ltd. founded in 2006.

QD solar cell technology, as a novel concept for cells, is still at an immature stage⁴, with plenty of room to explore, so that every endeavor is worth to be made in order to improve QD solar cell performance.

The performance of lasers, solar cells or any other device based on InAs/GaAs QD will be influenced by the properties of QDs, which are intrinsically related to their size, shape, and composition [61,62], so that the ability to control such properties will condition the final device performance. Most efforts on controlling the QD properties have commonly been focused on the growth conditions leading to a good understanding of the QD growth mechanism. Indeed, the growth rate [63–66] and temperature [67], as well as the time interval between the interruption of the QD growth and the capping process [68] play a main role affecting the final characteristics of InAs QDs. On one side, lower growth rates lead to larger dots with a lower surface/volume ratio and improved crystalline quality [64–66]. On the other side, lower growth temperatures result in a reduced In segregation during the capping process yielding larger QDs and a thinner wetting layer (WL) [69], which, in its turn, influences the QD electronic properties [70,71]. Less attention has been paid, however, to the capping process, which has been found to significantly affect the final QD properties. Indeed, the deposition of GaAs leads to a considerable dissolution of the QDs, significantly altering their structural properties [69,72–77]. Several processes taking place during capping, such as In segregation or In-Ga intermixing, are responsible for this phenomenon. The use of alternative capping materials, strategy commonly employed to extend the QD emission wavelengths, may exert a different impact on the evolution of the QD structure during the capping process, depending on the capping material nature. This means that, however accurate the QD growth conditions are, the QD size and shape will be finally determined by the capping process and, since this is a necessary step for any device application, the ability to understand and control it is of major relevance. Moreover, modified capping layers (CLs) would allow the manipulation of the QD-CL band offsets, as well as of the accumulated strain, allowing for the realization of band-structure and strain engineering at the nanoscale.

1.2. Objectives of the thesis

The main goal of this thesis is the study of the optical and structural properties of InAs/GaAs QDs capped with a thin GaAs(Sb)(N) layer and their implementation in both light-emitting and photovoltaic devices. With this aim, the research work was broken down into different main tasks focused on partial objectives as described below:

⁴ So far, there is no company marketing epitaxially grown QD-based solar cells. Nevertheless, it is noteworthy that, despite the still low conversion efficiency of semiconducting metal chalcogenide QDs, their low-cost manufacture via high-production solution-phase chemistry methods led Quantum Materials Corporation to bet on this technology for replacing silicon wafer-based solar cells. With this aim, the company founded Solterra Renewable Technologies, Inc. in 2007.

- (1) Study on the impact of the capping rate on the size, shape, and optical properties of standard GaAs/InAs/GaAs QDs.
- (2) Implementation of GaAsSb/InAs/GaAs QDs in LD devices and analysis of the impact of the Sb content and the band alignment on the device performance.
- (3) Implementation of GaAsSb/InAs/GaAs QDs in photovoltaic devices and analysis of the impact of the Sb content and the band alignment on the device performance.
- (4) Growth optimization of GaAsSbN/InAs/GaAs QDs for an independent tuning of the conduction and valence band structure.
- (5) Implementation of optimized GaAsSbN/InAs/GaAs QDs in photovoltaic devices and analysis of the impact on the device performance.

1.3. Structure of the thesis

Chapter 2 gives an introduction to the basic theoretical concepts regarding quantum confinement and, particularly, QDs. This chapter also presents an experimental background on InAs QDs and a brief discussion on their optoelectronic applications.

Chapter 3 describes the experimental techniques used during the research work in this thesis.

The experimental results will be organized into three major sections, set out according to the capping material used in the study:

Part I. GaAs/InAs/GaAs quantum dots: Chapter 4 presents the experimental results concerning the objective (1).

Part II. GaAsSb/InAs/GaAs quantum dots: Chapter 5 and 6 present the experimental results concerning the objectives (2) and (3), respectively.

Part III. GaAsSbN/InAs/GaAs quantum dots: Chapter 7 and 8 present the experimental results concerning the objectives (4) and (5), respectively.

Chapter 9 summarizes the most relevant conclusions concerning the experimental results in the thesis work while Chapter 10 outlines the potential directions for future research work.

Two appendices will bring the thesis to an end. Appendix A presents additional experimental work on GaAs(Sb)(N) superlattices, opening a new line of research intended for

multi-junction solar cells. Appendix B shows the list of publications, contributions to conferences, and awards related to this thesis work.

2 Self-assembled quantum dots

This chapter takes up the fundamentals of quantum confinement and basic models for QDs. The epitaxial growth of InAs QDs through Stranski-Krastanow mechanism and the thermodynamically imposed limitations on their real properties are then dealt with, discussing strain and band-structure engineering approaches commonly used to increase the tunability of QD properties. A brief introduction to their application in the field of LDs and solar cells is finally given.

2.1. Quantum confinement: Envelope function approximation

Electrons in macroscopic semiconductor crystals are described by means of the Schrödinger equation, which relates both the crystal lattice potential and the energy of the electron:

$$H\Psi = \left[\frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r}) \right] \Psi = \left[-\frac{\hbar^2}{2m_0} \Delta + V(\mathbf{r}) \right] \Psi = E\Psi, \quad (2.1)$$

where $\mathbf{p} = -i\hbar\nabla$ is the momentum operator, $\mathbf{r}$ the position vector, m_0 the free electron mass, and $V(\mathbf{r})$ the periodic lattice potential. According to Bloch's theorem, the solution for the Schrödinger equation in crystals are the so-called Bloch waves, with the form [78,79]:

$$\Psi = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (2.2)$$

where $\mathbf{k}$ is the wave vector of the electron and $u_{\mathbf{k}}$ is a Bloch function, with the spatial periodicity of the lattice crystal. Hence, Bloch waves are broken up into the product of a plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$, and a periodic Bloch function, $u_{\mathbf{k}}(\mathbf{r})$, combining the atomic and macroscopic character of the wavefunction in a crystal. The solutions for Schrödinger's equation are easily found assuming periodic lattice potentials as described by the Kronig-Penney model [80] and relates the energy eigenvalue with the magnitude of the $\mathbf{k}$ -vector through the effective mass in the crystal, m^* , with a parabolic expression:

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m^*}. \quad (2.3)$$

Imposing Born-von Kármán cyclic boundary conditions [81] determines the allowed values for the $\mathbf{k}$ -vector in the macroscopic crystal, which is given, for each direction of dimension L_i , by

$$k_i = \pm n_i \frac{2\pi}{L_i}, \quad (2.4)$$

where n_i are integers.

Fig. 2.1: Allowed states in momentum space (middle) and density of states as a function of the energy (right) according to the quantum confinement dimensionality.

In a macroscopic crystal, the energy states are so closely spaced that they can be treated as a continuous band. However, reducing the crystal dimensionality increases the separation of the allowed $\mathbf{k}$ values, so that a quantum treatment will be necessary in the case of structure dimensions d_i of the order of the de Broglie carrier wavelength. This is graphically represented in Fig. 2.1, showing the allowed states in momentum space (middle) and the density of states as a function of the energy (right) for a bulk crystal, and quantum-confined crystals in one, two, and three dimensions (QWs, quantum wires and QDs, respectively).

Nanostructures are usually hosted in a macroscopic material, forming a DHS at the nanoscale in which carrier wavefunctions are spatially localized. In this case, according to the envelope function approximation, the localized states in one-dimensional quantum confinement can be described as a linear combination of plane Bloch waves:

$$\Psi = \sum_j A(k_j) e^{i\mathbf{k}_j \cdot \mathbf{r}} u_k(\mathbf{r}) \approx u(\mathbf{r}) \sum_j A(k_j) e^{i\mathbf{k}_j \cdot \mathbf{r}}. \quad (2.5)$$

This description assumes that the Bloch function does not depend strongly on $\mathbf{k}$, which holds for the s-like and p-like functions at the band edge, so that $u_k(\mathbf{r}) \approx u(\mathbf{r})$ and the solution for the Schrödinger equation in confined structures can be expressed in the form:

$$\Psi = F(\mathbf{r})u(\mathbf{r}). \quad (2.6)$$

To obtain the envelope function $F(\mathbf{r})$, it is necessary to solve Schrödinger's equation for both the potential well (the nanostructure), F_w , and barrier regions (the host material), F_b . In the one-dimensional case:

$$\left(-\frac{\hbar^2}{2m_w} \frac{d^2}{dz^2} \right) F_w(z) = E F_w(z) \quad (2.7)$$

and

$$\left(-\frac{\hbar^2}{2m_b} \frac{d^2}{dz^2} + V_0 \right) F_b(z) = E F_b(z), \quad (2.8)$$

where m_w and m_b are the electron effective mass in the well and barrier, respectively, and V_0 the conduction band offset. The obtained envelope functions are sine or cosine waves in the well and an exponential decay in the barrier due to tunneling

$$\begin{cases} F_w(z) = A_w \cos(k_w z) \\ F_w(z) = A_w \sin(k_w z) \end{cases} \quad F_b(z) = A_b \exp \left[-k_b \left(z - \frac{L_z}{2} \right) \right], \quad (2.9)$$

where L_z is the confined structure dimension in z direction and k_w and k_b are the wave vector at the potential well and the barrier. Bound states energies can be obtained by imposing continuity at the well-barrier interface of both the function amplitude and the probability flux finding that the ground state confinement energy, as well as the energy spacing between subsequent bound states increases as the potential well width is reduced.

2.2. Quantum dots: Theoretical models

QDs can be modelled as a tetrahedral quantum box, in which three independent potential wells, as those described in Section 2.1, with a barrier energy V_0 are combined [78]. Three-dimensional Schrödinger equation in the QD can be generally written as

$$\left(-\frac{\hbar^2}{2m^*}\Delta\right)F_{QD}(\mathbf{r}) = EF_{QD}(\mathbf{r}). \quad (2.10)$$

Considering independent solutions in each orthogonal direction, we can separate variables

$$F_{QD}(\mathbf{r}) = F_{QD}(x)F_{QD}(y)F_{QD}(z), \quad (2.11)$$

following that

$$\frac{1}{F(x)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{F(y)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(y)}{\partial y^2} + \frac{1}{F(z)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(z)}{\partial z^2} = E. \quad (2.12)$$

Each term of the left side must be a constant, so we can write

$$\begin{cases} \frac{1}{F(x)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(x)}{\partial x^2} = E_x \\ \frac{1}{F(y)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(y)}{\partial y^2} = E_y, \\ \frac{1}{F(z)}\left(-\frac{\hbar^2}{2m^*}\right)\frac{\partial^2 F(z)}{\partial z^2} = E_z \end{cases} \quad (2.13)$$

where

$$E_x + E_y + E_z = E. \quad (2.14)$$

The same procedure applies in the barrier, separating variables, so that the system simplifies into three one-dimensional equations for each orthogonal direction, which solved as described in Section 2.1 leads to the overall envelope function and energy given by equations (2.11) and (2.12), respectively.

Real QDs are, in general, symmetric with a symmetry axis along the growth direction with a height much lower than the lateral size $L_z < L_x = L_y$. In this case, a higher confinement is found along the height direction L_z . Hence, the energy of the QD ground state, resulting from the addition of the ground states at each potential well, and denoted as (1,1,1) in Fig. 2.2, will be primarily determined by the QD height. A sufficiently larger lateral dot size will give rise to a doubly degenerated first excited state, denoted as (2,1,1) and (1,2,1), which is in agreement with experimental results showing an optical absorption rate from this state about twice that of the ground state [82,83].

Fig. 2.2: Electronic energy levels diagram for each spatial direction of the tetrahedral potential box representing a laterally symmetric QD with $L_z < L_x = L_y$. The harmonic wavefunction at each energy level inside the potential well and its exponential decay into the barrier are also represented. The resulting QD confined states are shown in the energy diagram on the right.

Although the simple quantum-box model describes the electronic structure of the QD in a first approximation, experimental observations may demand to resort in some cases to different models. For instance, it is necessary to consider a parabolic potential along the QD lateral dimensions in order to justify equally spaced confined energy states experimentally observed [84–86]. Advanced models are also available for a more accurate description of the electronic structure of the QD, such as $k \cdot p$ models, which allow obtaining the dispersion relation of a semiconductor. In particular, an 8×8 $k \cdot p$ model would take into account the interaction between the conduction and the three valence bands. Moreover, parameters such as the real geometry of the QD, the strain distribution and the piezoelectric field can also be

input in the model. Nevertheless, this simple picture in Fig. 2.2 clearly shows how the electronic structure of the QD will be mainly determined by its height, which is therefore a critical parameter.

In practice, the atomic-like electronic structure, arising from the three-dimensional quantum confinement, provides QDs with unique properties such as high radiative efficiency and thermal stability, among others, as will be discussed in the forthcoming sections.

2.3. Self-assembled quantum dots: Stranski-Krastanow growth mechanism

In an attempt to develop semiconductor QDs, efforts were initially focused on lithographic patterning techniques [87,88]. However, it was not until the growth of self-assembled QDs through epitaxial growth techniques [89,90] that QD-based devices could start to be fabricated and their properties experimentally tested. Although several fabrication techniques, such as colloidal chemical synthesis [91–94] or droplet epitaxy [95–98], are nowadays mastered, the fabrication of free-from-defect self-assembled QDs through epitaxial growth techniques continues to be the technique par excellence for the fabrication of QDs.

Fig. 2.3: Basic growth mechanisms: (a) Frank-van der Merwe mechanism (layer-by-layer growth), (b) Volmer-Weber mechanism (island growth), and (c) Stranski-Krastanow mechanism (layer-plus-island growth).

In 1958, Bauer developed the first classification scheme systematizing the epitaxial growth of thin films in terms of surface energies [99], going deeper into detail years afterwards [100]. In these terms, the epitaxial growth of thin films on a crystal surface may occur by means of three primary growth modes (Fig. 2.3):

- If the epilayer wets the substrate, the growth occurs by the so-called Fran-van der Merwe mechanism (layer-by-layer growth) [101]. In this case, the sum of the epilayer surface energy γ_B and the interface energy γ_{AB} is less than the substrate surface energy γ_A , $\gamma_B + \gamma_{AB} < \gamma_A$, so that the overall system energy is reduced by a layer by layer growth of the epilayer on the substrate.

- If the interaction among adatoms within the epitaxial layer is stronger than that among adatoms and substrate atoms, so that the epilayer does not wet the substrate, the growth occurs by the so-called Volmer-Weber mechanism (island growth) [102]. In this case, a layer by layer growth would lead to an increase of the overall system energy, so that the growth occurs, instead, in a three-dimensional regime, giving rise to the formation of islands on the substrate.
- An intermediate growth mechanism may occur, in which pseudomorphic layers form first, afterwards switching to the formation of islands (Fig. 2.4). This is the so-called Stranski-Krastanow mechanism (layer-plus-island growth) [30], by means of which epitaxially grown self-assembled QDs form. This is the typically observed growth mode in lattice-mismatched heteroepitaxial systems in which the pseudomorphic growth leads to an increasing accumulation of elastic energy γ_{el} with the layer thickness. In this case, the overall system energy progressively adds up until a critical thickness is reached in which $\gamma_B + \gamma_{AB} + \gamma_{el} = \gamma_A$, and the epilayer eventually relaxes via formation of islands. Once the three-dimensional structures nucleate, the islands coexist with the pseudomorphically grown layer, the so-called wetting layer (WL).

Fig. 2.4: Illustration of Stranski-Krastanow island formation during epitaxial growth of a material on a substrate with a lower lattice parameter ($a_{epi} > a_{sub}$). The epilayer grows pseudomorphically (top) until the critical thickness. Then, compressive strain elastically relaxes giving rise to the more energetically favorable three-dimensional growth (bottom).

2.4. InAs/GaAs quantum dots

InAs/GaAs QDs are the model system for the Stranski-Krastanow mechanism due to the large lattice mismatch between InAs and GaAs. The difference of $\sim 7\%$ in the lattice parameter induces such a large accumulation of strain that the formation of islands on a (001) GaAs surface arises for a very thin critical thickness within the range ~ 1.6 - 1.8 MLs [63,103–105]. Once capped with GaAs, InAs/GaAs QDs form a DHS GaAs/InAs/GaAs leading to the confinement of both electrons and holes within the islands. Such QDs show the type-I band alignment in Fig. 2.5 (a), depicted along the growth direction (z) across the center of the QD, as shown on Fig. 2.5 (b). As discussed in Section 2.2, the confinement energy of both electrons and holes will mainly depend on the QD height, so that the InAs QD ground state energy could be tuned according to the dependence on the QD height in Fig. 2.5 (c). However, typical mean sizes of GaAs/InAs/GaAs islands are ~ 20 nm base width and 3-4 nm height, what limits to a high extent the ground state energies achievable by these structures. These restrictions concerning the transition energy and the impossibility to control the band alignment highly limit the field of applications of standard InAs/GaAs QDs.

Fig. 2.5: (a) Calculated RT conduction and valence band edge profile in the growth direction (z) across the center of an InAs QD together with the energy of the electron and hole ground states as shown in [106]. (b) Dark-field transmission electron microscopy (TEM) image of a typical InAs/GaAs QD. The arrow indicates the growth direction (z). (c) Theoretical RT band gap energy as function of the QD height as reported by Yamauchi et al. [107].

Fig. 2.6 (a) shows the height of buried InAs QDs reported from different publications in which QDs were capped under standard conditions (~ 1 ML/s, 450-530 $^{\circ}\text{C}$). Remarkably, all the values are within the typical range (~ 3 -4 nm), despite the very different initial QD heights (QD height before capping), from 4.2 nm up to ~ 10 nm. Indeed, standard capping with GaAs entails a heteroepitaxial process which alters the ultimate thermodynamic equilibrium structure, leading to a considerable dissolution of InAs QDs as shown in Fig. 2.6 (b) and altering their structural properties [69,72–77]. A minimization of the additional strain introduced by

the GaAs capping layer through In-Ga intermixing is generally believed to be behind this dissolution process. Such a process seems to impose a generalized evolution towards the thermodynamic equilibrium during overgrowth whereby QDs are similarly levelled, regardless of the initial QD size.

Fig. 2.6: (a) Average height of InAs/GaAs QDs reported by different authors before (when available) and after the capping process (red and blue dots, respectively) [73,108–114]. A schematic of the QD dissolution process during capping is also represented in the inset, whereby the QD top flattens through surface In-Ga intermixing and surface diffusion of In leads to the WL thickening (orange layer). (b) The upper image shows a completely preserved QD, achieved by the application of a GaAsSb capping layer [113]. A typical QD capped with GaAs is shown on the lower image [108], where a flatter QD top and thicker WL are observed.

2.5. Modified capping layers (CLs)

The versatility of InAs/GaAs QDs can be enhanced by using modified CLs. On one hand, the use of strain-reducing CLs¹ has recently been the focus of intense efforts aimed to minimize the interface energy in order to reduce the strain-driven QD dissolution during capping

¹ Strain-reducing CLs, such as InGaAs or GaAsSb, have a lattice constant larger than that of GaAs (see Fig. 1.1). Hence, although the overall strain in the structure increases, the lower lattice mismatch at the QD-CL interface reduces strain within the QD.

[109,113,115–117]. On the other hand, this approach additionally allows tailoring the electronic structure of the QDs and the emission wavelengths of InAs QDs have been extended to the 1.3–1.55 μm region using InGaAs [40,118–120] and GaAsSb [41,42,106,121] strain-reducing CLs. In particular, the simultaneous realization of strain and band-structure engineering at the nanoscale by means of GaAsSb CLs is already well-known. Ulloa et al. [108] showed how the increase of the Sb content in a GaAsSb strain-reducing CL leads to a higher preservation of the QD height, as observed in Fig. 2.7. In good agreement with the model proposed by Grossi et al. [117], the QD height was found to follow a linear tendency with the Sb content, i.e., with the lattice parameter increase of the capping material.

Fig. 2.7: QD height normalized to the height of the equivalent uncapped QDs as a function of the Sb content in the CL as shown in [108]. A value of 1.0 indicates a completely suppressed decomposition process. The red dash-dotted line is a linear fit to the values before completely suppressing decomposition. The different background colors indicate the two different regimes.

Besides the progressive inhibition of the QD dissolution, the addition of Sb is known to mainly affect the valence band of GaAs, so that the QD ground state transition energy can be lowered through the independent tuning of the hole confinement [106]. This particular case highlights the power of this approach, additionally allowing for the transition from a type-I (Fig. 2.8 (a)) to a type-II (Fig. 2.8 (b)) band alignment in zero-dimensional structures, which takes place for an Sb content $\sim 16\%$. While in type-I structures, holes are confined inside the QD (Fig. 2.8 (c)), for Sb contents above this percentage, the hole wavefunction is located in the CL towards the base of the QD in the [110] direction, as shown in Fig. 2.8 (d). The inhomogeneous strain pulls the hole wavefunction towards the QD rim at its base, while the piezoelectric field squeezes the wavefunction along the [110] direction. Indeed, the delocalization of the heavy hole wavefunction towards the CL takes place progressively with the amount of Sb. The consequence is that, even in the type-I band alignment, in which the

holes are located inside the QD, the maximum of the probability density of the hole wavefunction split in two parts located close to the QD-CL interface in the $[110]$ direction (Fig. 2.8 (c)). The paramount role of the band alignment in the optoelectronic properties will be evidenced throughout this work.

Fig. 2.8: Conduction and valence band edge profile in the growth direction (z) across the center of an InAs QD capped with GaAsSb showing type-I (a) and type-II (b) band alignments as shown in [106]. (c) and (d) show the respective distribution probability of the ground state hole wavefunction in the $(1 -1 0)$ plane.

It has been demonstrated that the strain field surrounding the QD is not the only parameter affecting the dissolution of QDs. The use of GaAsN strain-compensating CLs² is of particular interest, since the QD erosion during the overgrowth is reduced despite the larger lattice mismatch between the QD and the GaAsN CL [109]. Stronger Ga-N bonds as compared to those of Ga-As are believed to reduce intermixing and surface diffusion during capping, increasing the final QD height. Moreover, the incorporation of N in GaAs, according to the band-anticrossing (BAC) model [122], reduces the band gap through only lowering the conduction band of GaAs. This allows extending the emission of InAs QDs towards the telecommunication wavelengths [110,123], while switching the band alignment to a type II

² Strain-compensating CLs, such as GaAsN, have a lattice constant lower than that of GaAs (see Fig. 1.1). Hence, strain within the QD is enhanced by the higher lattice mismatch at the QD-CL, while the overall strain in the structure is reduced.

structure for relatively low N contents [109]. Moreover, N-containing CLs act as strain-compensating layers, which is critical to avoid defect formation due to accumulated strain in multi-QD-layer stacks [124]. These particularities make the combination of Sb and N in a quaternary CL of particular interest. Although different quaternary alloys such as InGaAsN [43,125], InGaAsSb [126], or AlGaAsSb [127] have recently been used as CLs on InAs/GaAs QDs providing different kinds of advantages, none of them provides the versatility of GaAsSbN CLs in terms of band-structure engineering and strain compensation. Indeed, the use of quaternary GaAsSbN CLs on InAs/GaAs QDs allows an independent tuning of the electron and hole confinement potentials, as has already been demonstrated [128] (see Fig. 2.9). The band alignment can therefore be switched from type I to type II with different configurations: holes or electrons localized outside the QD for high Sb or N contents, respectively.

Fig. 2.9: Sketch of the expected band structure in the growth direction (z) in InAs/GaAs QDs capped with GaAs, GaAsSb, GaAsN, and GaAsSbN from left to right.

2.6. InAs/GaAs quantum dot applications

As the most widely mastered QD system, InAs/GaAs QDs are nowadays researched for an increasing broad range of applications. This section takes up a brief discussion on those applications of interest in this thesis: QD lasers and QD solar cells.

2.6.1. Quantum dot lasers

The three-dimensional confinement in QDs focuses the injected carriers in a narrower range of energies than in bulk and QWs, leading to a faster carrier filling at the operation current densities. This reduces the transparency current density leading to an also lower J_{th} while resulting in a faster optical gain increase with the injection current [33]. The reduced inhomogeneous broadening leads to an α -factor in QD lasers a few times lower than in QW lasers [129,130], which is of great relevance for high-modulation speed [131–133]. Besides the predicted and achieved improvements in J_{th} and gain of LDs, QDs provide lasers with

a higher thermal stability. Indeed, J_{th} is expected to be completely temperature-independent in QD lasers [32], since the thermal spreading of carriers vanishes in QD structures, whose density of states is delta-function-like.

These unique properties of QDs have attracted immeasurable efforts focused on achieving more efficient QD-based lasers at the longer telecommunication wavelengths. InAs QD devices lasing beyond 1.55 μm were achieved using InP substrates in the earlier 2000 [134,135] and more recently this system allowed achieving lasing wavelengths near 2 μm [136]. However, the J_{th} achieved in InAs/InP QD lasers are still far from those achieved in InAs/GaAs QD lasers at the 1.3 μm telecommunication wavelength. The ability to extend the lasing wavelength of InAs/GaAs QDs by using modified CLs maintains the hope of achieving more efficient QD lasers at the 1.55 μm telecommunication wavelength while taking advantage of the additional benefits of this system, as discussed in Section 1.1. Moreover, the implementation of type-II structures in LDs, still almost unexplored, could be exploited in order to achieve additional wavelength and gain tunability [137–139], an inhibition of spontaneous emission and Auger recombination or higher thermal stability [138].

2.6.2. Quantum dot solar cells

According to the detailed-balance model developed by Shockley and Queisser [55], the final photovoltaic conversion efficiency is conditioned upon the balance between the absorption and emission processes in the solar cell. For their model, Shockley and Queisser mainly assume the only absorption of photons with energy above the semiconductor band gap, the generation of one electron-hole pair from each absorbed photon, and the thermalization of both electron and hole populations with the lattice temperature. Both transmission of photons with energy lower than the band gap and thermal dissipation are responsible for power conversion losses above 50% [140]. Among the broad spectrum of approaches, QDs represent one of the recent novelties conceived to exceed the Shockley-Queisser limit efficiency of conventional solar cells. The unique optoelectronic properties of QDs arising from the atomic-like density of states have been recognized to be of potential benefit in the implementation of different QD-based technologies, as discussed in Section 1.1. The most immediate advantage of using InAs QDs, regardless of the nature and design of the solar cell, is the ability to extend the absorption spectrum towards the near infrared (Fig. 2.10). A QD solar cell is therefore very similar to that proposed by Barnham and Duggan, who predicted an efficiency improvement with the introduction of QWs in the host material [141]. QDs also find application in the so-called intermediate-band solar cells. This concept, once proposed by Wolf in 1960 [142], is based on the idea of introducing a band of impurities within the band gap in order to allow for additional electronic transitions and was not until the late 1990's when Luque and Martí found an attracting opportunity in QDs [54].

Despite the expected advantages of QD solar cells and, although an increase in J_{sc} is the most direct achievement, the introduction of QDs into the host material also entails some drawbacks that must be addressed. On one hand, the strong carrier localization and the efficient radiative recombination in the QDs hinder an efficient collection of photogenerated carriers. Indeed, the addition of QDs also leads to an V_{oc} loss, which may be significant. On the other hand, the small absorption volume results in rather poor contribution from QDs, which demands the stacking of a high number of QD layers in order to enhance their contribution to the total cell current. This leads to the accumulation of strain inducing the origination of extended defects, increasing likelihood of carrier losses and further affecting V_{oc} , limiting the maximum number of QD layers that can be incorporated in the devices.

The J_{sc} of a QD solar cell could be further enhanced by the application of a thin CL of a certain nature, which in practice is a QW that tunes the QD optical properties. Such a hybrid QD-QW solar cell would offer not only a means to accurately tune the effective absorption edge, in order to harvest a broader solar spectrum (Fig. 2.10), but also the possibility to compensate the drawbacks mentioned above. Indeed, this approach would enable a huge versatility in terms of the solar cell design allowing, for instance, for the realization of QD solar cells with type-II band alignments. This would increase radiative lifetimes and could result in an improved carrier extraction and subsequent collection. In addition, strain-balancing techniques would also be possible with the use of material CLs with a lattice parameter lower than that of the host material.

Fig. 2.10: AM1.5G solar spectrum (black curve) showing the portion of light converted to electricity by GaAs after carrier thermalization (blue-shaded curve). The shaded area beyond GaAs absorption edge represents the additional range of the solar spectrum achievable by InAs QDs (green) and InAs QDs tuned with a CL (red).

3 Experimental techniques

In this chapter the main experimental techniques used during the thesis work are described. The epitaxial growth equipment and the in-situ growth characterization are first addressed. The subsequent sections will deal with the optical and structural characterization of the samples, the device processing, and the characterization of the optoelectronic and photovoltaic devices.

3.1. Epitaxial growth of samples: Molecular Beam Epitaxy (MBE)

The relevance of the MBE growth technique has already been emphasized in Section 1.1. There, it has been shown how important its role has been in the development of more efficient devices thanks to the high crystalline quality and the high level of control over the thickness of an epitaxially grown layer to the atomic order. This is possible thanks to the use of an ultra-high vacuum (10^{-8} - 10^{-12} Torr) growth chamber in which the epitaxial growth is carried out at slow growth rates. In an MBE growth chamber, solid or liquid elemental materials with a high purity are used as material source. These, set at a specific temperature, sublime/evaporate forming molecular beams that impinge the sample growth surface, heated at the growth temperature. Upon landing on the surface, atoms condense and build up in epitaxial layers. The mechanisms taking place on the surface during MBE growth are complex and their description is beyond the scope of this thesis. A detailed description of the MBE growth of GaAs and related compounds can be found in the work of Herman and Sitter [143] and in the more recently published work of Orton and Foxon [144].

Fig. 3.1 shows a schematic of the MBE growth chamber used in this thesis and located in the clean room of ISOM. The MBE system is a Riber 32 equipped with Knudsen diffusion cells for Ga, In, Al, Sb, Si and Be. A cracking cell is used for As supply by means of a needle valve. Contiguously to the valve, the cracker allows As molecules to pass into the growth chamber avoiding their condensation and can be used to crack As_4 molecules into As_2 at convenience. A radio frequency plasma source is required, instead, to supply active N from a N_2 pure source, whose access into the growth chamber is controlled by hermetic valve. The molecular beams strike the substrate surface, placed on the adjustable manipulator, giving place to the crystallization process. Before the growth, the beam equivalent pressure of each element is accurately set, if available, with the help of a Bayard-Alpert gauge. The MBE is additionally equipped with a Reflection High-Energy Electron Diffraction (RHEED) system, which will provide a detailed monitoring of the growth procedure. During the growth, the chamber is cooled down with liquid N, introduced in the cryogenic panel of the growth chamber, in order to further lower the pressure within the MBE chamber.

Fig. 3.1: Schematic view of the MBE growth chamber used in this thesis.

3.1.1. In-situ characterization: Reflection high-energy electron diffraction (RHEED)

RHEED is a powerful technique which enables to determine the crystalline structure of a surface and to monitor in-situ the evolution of the surface during the growth. RHEED geometry is relatively simple (Fig. 3.2 (a)). It consists of an electron beam which strikes the surface of the sample at a low incidence angle (typically $1-4^\circ$), in order to limit the penetration depth of electrons, so that it is more sensitive to the first atomic planes. The electrons are diffracted by the surface and detected by a fluorescent screen, perpendicular to the sample plane, where a diffraction pattern characteristic of the surface crystalline structure is formed. This will be very useful to accurately determine the growth temperature during the growth. Indeed, GaAs undergoes a phase transition at $\sim 510^\circ\text{C}$, commonly used as a reference for the growth temperature of the active layer. At such a temperature, the RHEED pattern switches from a (2×4) , at higher temperatures, into a cubic (4×4) diffraction pattern, at lower temperatures (Fig. 3.2 (b) and (c), respectively) and vice versa.

Fig. 3.2: (a) Schematic illustrating the formation of a RHEED pattern on a fluorescence screen. (b) and (c) are (2x4) and cubic (4x4) diffraction pattern of GaAs above and below $\sim 510^\circ\text{C}$, respectively.

RHEED additionally allows calibrating the growth rate of GaAs due to the oscillations on the diffraction pattern intensity observed during the growth. Neave et al. [145] proposed that the minimum of intensity would correspond to the formation of half an epitaxial monolayer (ML), increasing to its maximum once the growing layer is complete. The intensity would oscillate with the periodicity in which consecutive layers are deposited, giving a direct estimation of the growth rate in MLs^{-1} . Strictly speaking, things are unusually so simple and the intensity oscillations decay in practice towards zero amplitude over some number of periods. Joyce et al. [146] proposed a model describing a growth mechanism in a try to explain this phenomenon (Fig. 3.3). They mainly assumed that after the partial growth of one ML on the surface, a second layer would nucleate before the former one is complete. The nucleation of subsequent layers would lead to a rougher surface, reducing the maximum intensity of the diffraction pattern until eventually an equilibrium would be established in the growth mechanism. Hence, the growth rate would be more accurately defined by RHEED oscillations at this equilibrium growth regime.

Fig. 3.3: Image taken from the work of Joyce et al [146], showing the proposed evolution of the film in terms of the number (θ) of MLs deposited, starting from a perfectly flat surface, and its correlation with the RHEED intensity.

3.1.2. Sample preparation and growth procedure

Fig. 3.4 shows a global view of the MBE system used for the present thesis work and located at ISOM. Besides the Riber 32 main growth chamber (left), the system consists of

an intermediate spherical chamber, devoted to Ar ion beam dry etching, and an introduction chamber (right), all of them isolated from one another.

Fig. 3.4: Global view of the MBE system at ISOM facilities.

The MBE system is prepared for In-free substrate holders designed to mechanically hold quarters of 2-inch diameter wafers. In this thesis, all the substrates were obtained by cleaving commercial n^+ Si-doped (001)-oriented GaAs wafers into four quarters. Once the substrates are cleaved and placed onto the holder, this is placed into the introduction chamber, where substrates are subjected to a first degas process at $\sim 350^\circ\text{C}$ for 2 hours in order to desorb dirt and water particles adsorbed on the substrate surface. Then, substrates are introduced into the MBE growth chamber by means of a transferring holder. Within the growth chamber, the substrate holder is placed on the holder manipulator, which can be rotated in order that the substrate faces equidistantly the Knudsen cells for the epitaxial growth. The growth chamber is then isolated and the substrate subjected to As_4 overpressure in order to avoid As desorption. Before the epitaxial growth, the substrate temperature is slowly risen up to $\sim 590^\circ\text{C}$ in order to desorb the native oxide coating [147,148]. This process is monitored with RHEED, switching in some minutes from a dim pattern, corresponding to the amorphous oxide layer, into the (2x4) pattern relative to high-temperature As-stabilized (001) GaAs surface (Fig. 3.2. (b)). Once the oxide is desorbed, the holder manipulator, equipped with an automatic rotation mechanism, turns continuously around the substrate plane axis during the growth in order to provide a homogeneous growth all over the substrate. The substrate temperature is slightly reduced up to the growth temperature, $\sim 580^\circ\text{C}$, and thin GaAs films are

first intermittently grown (10 ML GaAs/10 s growth interruption) in order to check the substrate surface smoothing until a sharp and clear RHEED pattern is achieved. Once a smooth surface is achieved, RHEED is used to calibrate the growth rate of GaAs as described in Section 3.1.1, which is set to the typical rate of 1 MLs^{-1} for the growth of a thick high-crystalline quality GaAs buffer before depositing the QD layer. The substrate temperature is cooled down up to the appropriate growth temperature of InAs QDs taking as reference the temperature of the RHEED pattern transition from (2×4) into cubic (4×4) as shown in Fig. 3.2. The As_4 overpressure is slightly reduced for a more suitable growth of the QDs [67], for what an amount of InAs higher than the critical thickness ($\sim 1.6\text{-}1.8 \text{ MLs}$) is deposited. During the deposition of InAs, once the critical thickness is reached, the transition from a streaky into a spotty diffraction pattern, as shown in Fig. 3.5, reflects the relaxation of the epitaxial layer, allowing for an accurate control over the InAs deposition rate and, therefore, over the overall deposited amount of InAs. After their formation, QDs are capped applying a thin CL of a specific material rising then the substrate temperature up to $\sim 580^\circ\text{C}$ for the growth of a thick GaAs layer, which will end the structure or serve as a spacer layer before the growth of a new QD layer. Further particular details on the growth procedure will be described for each specific set of samples in the respective experimental sections.

Fig. 3.5: Spotty RHEED pattern observed during the relaxation of an InAs 2D epitaxial layer into 3D growth mode.

3.2. Optical characterization: Photoluminescence (PL)

Photoluminescence (PL) is a non-destructive optical characterization technique through which light emission from a sample is initiated by photoexcitation. The sample is excited using a laser with photon energies higher than the material band gap, generating electron-hole pairs by the promotion of electrons from the valence band to the conduction band. Before recombination, electron-hole pairs rapidly thermalize via phonon-scattering and Coulomb interaction. This occurs in bulk GaAs within the first 100 fs after excitation [149].

After a certain residence time, radiative recombination leads to the emission of photons with the optical band gap energy.

Electron-hole pairs may also recombine non-radiatively via Auger recombination [150] or through a Shockley-Read-Hall (SRH) process [151,152], reducing the radiative emission efficiency and therefore the PL intensity. The SRH mechanism will become relevant under the presence of impurities or defects, which introduce additional energy levels within the band gap, giving rise to the formation of deep-level traps where non-radiative recombination will primarily occur. Hence, PL allows a first evaluation of grown structures correlating their optical properties with the structural quality.

In the case of QDs, the energy of the PL emission peak is directly related to the QD size and composition, since it reflects the ground state transition energy. Instead, the full width at half maximum (FWHM) provides information concerning the QD size distribution homogeneity. Regarding the integrated intensity, it allows evaluating the PL emission efficiency and its evolution with temperature, providing additional information concerning the process giving rise to the PL emission attenuation with temperature. In case there is a single dominant process affecting it, the evolution of the PL with temperature can be described by an Arrhenius-like dependency and the thermal activation energy related to such a process drawn [153]. This energy may be associated to the escape of either or both carriers to the respective barriers, in which case the impact of a certain CL can also be analyzed [106]. Additional information can be obtained from the evolution of the PL with temperature in QDs, sometimes characterized by an unusual reduction of the FWHM [154–157], due to carrier redistribution among the predominant QDs. Also PL measurements as a function of the incident light power density are useful to characterize QD-CL structures giving, on one hand, information on the excited states. On the other hand, such measurements allow determining QD-CL the band alignment. Indeed, no effect on the PL peak energy is expected in type-I structures, while it follows a linear dependence on the third root of the excitation power in type-II structures, arising from the band bending effect induced by the spatially separated photo-excited carriers [158].

All the PL measurements shown in this thesis were conducted at the ISOM facilities. The used infrared PL setup is shown in Fig. 3.6. A continuous He-Ne laser emitting at 632.8 nm is used as the excitation source. A set of lenses and mirrors is used to focus the laser beam onto the sample. The sample is placed in a closed-cycle helium cryostat, which allows performing PL measurements at 15 K. The emitted light is driven to a 1 m-grating monochromator, dispersed, and finally detected with a liquid nitrogen-cooled Ge photodetector. A high-pass filter is placed at the monochromator entrance in order to avoid the passage of light from the laser and the detection of its second-order diffraction. An optical chopper is employed to achieve a pulsed light beam in order to reduce signal noise with a lock-in amplifier. The sample emission intensity is finally recorded at each wavelength. For PL measurements

as a function of the incident light power density, an attenuating filter is placed at the laser output, whose power is calibrated with a Liconix 45PM laser power meter.

Fig. 3.6: Schematic of the infrared PL setup used at the ISOM facilities.

3.3. Structural characterization

3.3.1. Cross-sectional scanning tunneling microscopy (X-STM)

Cross-sectional scanning tunneling microscopy (X-STM) is a unique technique, nowadays available only in a few laboratories in the world, to explore buried nanostructures at the atomic scale. X-STM has been increasingly used to successfully characterize nanostructured III-V materials [159–162] using an atomically sharp metallic tip to scan the cleaved surface of the conducting material kept in vacuum. The tip is approached to the surface within a distance on the order of the nanometer so that the application of a small bias voltage yields a tunnel flow of electrons through the vacuum barrier between tip and surface. The tunneling current depends on the wavefunction overlap between tip and sample surface states, as described by Bardeen’s perturbation theory [163]. In a first approximation, the current tunneling through the junction is given by [164]:

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_s(E_{F_s} + \epsilon) \rho_t(E_{F_t} - eV + \epsilon) |M|^2 d\epsilon, \quad (3.1)$$

where ρ_s and ρ_t are the local density of states (LDOS) of the sample and the tip, respectively, E_{F_s} and E_{F_t} the Fermi energy of the sample and the tip, respectively, e the electron charge, V the applied bias voltage, and M the tunnel matrix element between the tip and sample

states, which represents the wavefunction overlap of the charge carriers in the tip and the sample. Tersoff and Hamann successfully applied Bardeen's formula in the interpretation of X-STM images modelling the tip as a locally spherical system of free electron gas confined in the tip body [165]. The simple treatment of the tip as a spherical potential well and the sample surface wavefunction as planar sinusoidal waves with decaying amplitude into the vacuum was found to be in good agreement with experimental results. Assuming a point-like tip with an s-state wavefunction, the matrix element can be approximated by [165]:

$$|M|^2 = \exp(-2\kappa d), \quad (3.2)$$

where $\kappa = \hbar^{-1}(2m\phi)^{1/2}$ is the inverse decay length for the wavefunctions in vacuum, where ϕ is the work function. Assuming the simplification of a constant LDOS at the X-STM tip and the low-temperature approximation for the fermionic distribution to be valid, equation 3.1 can be simplified to

$$I \propto \int_0^{eV} \rho_s(E_{F_s} + \epsilon) \exp(-2\kappa d) d\epsilon. \quad (3.3)$$

At constant voltage, the dependence of the tunneling current on the distance between tip and sample surface can be reduced to:

$$I \propto \exp(-2\kappa d). \quad (3.4)$$

The fast exponential-like decay allows X-STM achieving an out-of-plane resolution even beyond 0.01 nm. Hence, if the surface is scanned by the tip while keeping the tunneling current constant using a feedback loop, an accurate atomically resolved topographic map of the surface can then be acquired from the LDOS isosurface. This mode of operation of the X-STM is called constant-current mode and is schematically represented in Fig. 3.7. There are two possible imaging conditions in X-STM operating at constant current mode, depending on the polarity of the applied bias: filled state imaging at negative bias, the electrons tunneling from the sample into the tip via group-V elements, and empty state imaging at positive bias, the electrons tunneling from the tip into the sample via group-III elements. Hence, a map of the group-III or group-V elements is obtained according to the bias conditions. Such maps will also be influenced by an electronic contrast altering the apparent surface topography. Nevertheless, this can be avoided by applying a high absolute tunnel voltages [166]. In addition, the use of current-image mode, which records tunnel current variations during the feedback loop controlling the tip-sample distance, is useful to determine the exact outline of embedded nanostructures, which may be obscured by the outward relaxation.

Fig. 3.7: Schematic of the STM operation under constant-current mode.

The previous assumption of a constant LDOS at the STM tip and the validity of the low-temperature approximation provide a straightforward method to retrieve electronic information through the first derivative of the tunnel current. From equation 3.3, it immediately follows that

$$\frac{dI}{dV} \propto \rho_s(E_{F_s} + \epsilon) \exp(-2\kappa d). \quad (3.5)$$

This means that, if the tip-sample distance keeps constant, the conductance is directly proportional to the LDOS of the sample surface. The plot of the conductance as a function of the applied bias will therefore allow determining the local band gap.

The X-STM measurements shown in this thesis were performed at the Photonics and Semiconductor Nanophysics group in the Technical University of Eindhoven (The Netherlands), during a 3-month stay at the group of professor P. M. Koenraad. The measurements were conducted at liquid nitrogen temperature (77 K) on a (110) surface plane of the samples, which was obtained by in-situ cleavage under ultra-high vacuum conditions ($p < 4 \cdot 10^{-11}$ Torr). Filled state topography images were obtained in constant current mode (50 pA) at high negative voltages (-3 V), using polycrystalline tungsten tips.

Tips are prepared electro-chemically from a 250 μm -diameter polycrystalline tungsten wire (Fig. 3.8 (a)). Part of the wire is placed within a 2 molar KOH solution, using a platinum-iridium (90%/10%) spiral as a counter electrode, and a positive voltage is applied to the tip-wire, driving the following oxidation process:

The reaction product WO_4^{2-} drops down along the tungsten wire, covering and shielding the submerged part of the wire. This leads to a faster reaction at the meniscus, necking the wire at the surface of the solution, so that the tip eventually breaks at the neck point, leaving a very sharp tip (Fig. 3.8 (b)).

Fig. 3.8: (a) Schematic of the tungsten tip preparation procedure and (b) a scanning-electron-microscopy image of a tungsten STM tip.

Once the tips are ready, they are baked in the preparation chamber at approximately 250 °C and then subjected to a glowing procedure in order to remove the oxide on the surface. Finally, tips are mechanically stabilized by means of an argon bombardment.

Regarding the samples, rectangular pieces of typical sizes around 3.5×9 mm are cleaved from the wafer of interest. A metallic contact is deposited on top of the sample for a good electrical contact between sample and holder. Then, samples are thinned by polishing with aluminum oxide powder on the back side to a thickness of about 100 μm for an easy cleavage inside the X-STM chamber. A scratch is made on the sample for the cleavage nucleation and then the sample is clamped in the holder with the use of molten slices of indium, which provide an even pressure on the sample and a fixed electrical contact. After a baking process inside the preparation chamber, clean samples are transferred to the X-STM chamber, where they are cleaved by gently pushing the sample with a wobble stick.

3.3.2. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which, basically, a beam of electrons is accelerated by a high potential voltage (typically 100-300 kV) and transmitted through an ultra-thin specimen. After the interaction between electrons and sample, transmitted electrons are used to form an image. The suitable thickness will depend on the nature of the material under study and the energy of the accelerated electrons. In case of conducting high-resolution TEM (HR-TEM) measurements, by which individual atomic columns of the crystal are resolved, thicknesses below the mean free path λ_{mfp} , commonly below 100 nm, will be required [167].

Fig. 3.9 shows a schematic of a transmission electron microscope which essentially consists of a columnar vacuum chamber containing the illumination system: an electron gun, usually a tungsten filament; a set of electromagnetic lenses consisting of condensing lenses, objective lenses and projecting lenses; a projection screen, onto which the magnified image is focused; and an image recording system.

Fig. 3.9: Schematic of a transmission electron microscope.

The primary electron beam coming from the electron gun strikes on the thin specimen, through which a large part of the electrons is transmitted. Some of the transmitted electrons are not altered at all by the sample while some others are scattered by the atoms of the material, the electron beam behaving as a spherical wave propagating through the sample. On the basis of this, there are two different modes of image formation in TEM: in case the image is formed from the transmitted beam which has not undergone dispersion, the object image is dark on a bright background. If, on the contrary, the image is formed from the scattered electrons, the image appears bright on a dark background. These two techniques are consequently called bright-field and dark-field imaging, respectively. While dark-field imaging mode will provide essentially chemical information, bright-field imaging will help visualize defects in the crystalline structures.

Most of the nanostructures grown and analyzed in this work are embedded between thick layers, so that they require a previous polishing process for TEM measurements. Both sample preparation and all the TEM measurements presented in this thesis were carried out at Departamento de Ciencia de los Materiales e IM y QI, Universidad de Cádiz (Spain), by the group of professor D. González. Conventional TEM measurements for dark-field and bright-field imaging were performed using a JEOL JEM-2100 LaB6 microscope operating at 200 kV. Besides conventional TEM, high-resolution high-angle annular dark-field (HRHAADF) imaging was performed in a X-FEG FEI TITAN cross-sectional scanning-tunneling electron microscope operating at 300 kV, equipped with a spherical aberration corrector for the electron probe.

3.3.2.1. Energy-dispersive X-ray spectroscopy (EDX)

When a sufficiently accelerated electron beam strikes on the surface of a solid, it can cause the ionization of the present atoms, so that when an electron of an outer shell falls to the inner empty state, it may produce the emission of both X-ray electromagnetic radiation and Auger electrons. Both phenomena compete with one another and the likelihood for X-ray emission to occur, instead of the emission of an Auger electron, is given by the fluorescence yield (ω).

The emission of X-ray is identified as a function of the shell in which the expulsion of an electron occurred ($K, L, M, N \dots$), the provenance shell of the new electron taking the place of the first one ($\alpha, \beta, \gamma \dots$), and its energetic subshell (1,2,3...). The fluorescence yield of the K shell, ω_k , increases progressively with the atomic number of the emitting element. The most accepted approximation to express this relation is the one proposed by Burhop, which, in its simplest version, takes the form [168]:

$$\omega_k = \frac{Z^4}{a + Z^4}, \quad (3.6)$$

where a is a constant related to screening effects. It follows that in elements with low Z , the X-ray signal will be too weak, so that it is not a proper technique to measure the concentration of light elements.

The analysis of the characteristic X-rays emitted from the sample allows knowing its composition, which simply consists of measuring the wavelength or the energy of the produced photons. The two types of systems which are nowadays utilized in modern equipment for the performance of such measurements are the wavelength dispersive X-ray spectrometer (WDX) and the energy dispersive X-ray spectrometer (EDX). WDX allows for a higher precision in quantifying the composition of an element, as well as a higher spectral resolution. Moreover, it allows the quantification of elements with $Z > 4$ (*Be*), while the limit for EDX is $Z > 11$ (*Na*). Nonetheless, data acquisition time is much faster in EDX.

The EDX measurements in this work were performed at Departamento de Ciencia de los Materiales e IM y QI, Universidad de Cádiz (Spain) in the JEOL JEM-2100 LaB6 microscope mentioned previously.

3.3.3. High-resolution X-ray diffraction (HR-XRD)

While electrons can be scattered by the nuclei of atoms as well as by the electrons of those, X-ray can only be scattered due to the interaction of the negatively charged electrons with the incident radiation field. At the time of the interaction, electrons oscillate at the frequency of the incident radiation, afterwards reemitting secondary spherical waves. X-ray scattering by an atom is the additional result of scattering by all the electrons of the atom. When elastic scattering occurs in a crystal lattice (Fig. 3.10), where the atoms are periodically arranged, X-ray are diffracted in such a manner that they present a specific phase relation among them such that a destructive interference occurs in most directions. Meanwhile, constructive interference takes place in a few concrete directions, in which the difference between the path lengths of rays diffracted on successive crystallographic planes equals an integer multiple of the incident radiation wavelength, giving rise to the origination of scattered rays. That is, the interference of diffracted X-rays produces dispersion effects structured in peaks of maximum intensity. The reciprocal lattice of the crystalline structure defines these peaks, which are said to fulfill Bragg diffraction conditions, determined by the law named after him:

$$2d_{hkl} \sin \theta = n\lambda, \quad (3.7)$$

where d is the distance between hkl atomic planes, θ is the angle of incidence, n is a whole number, and λ is the wavelength of the X-rays.

Fig. 3.10: Schematic showing the constructive interference of an incident X-ray beam diffracted by the parallel lattice hkl planes.

A thick layer grown on a certain substrate can therefore be characterized through X-ray diffraction (XRD) measurements by a related diffraction Bragg angle shifted with respect to that of the substrate as a function of its lattice parameter. Since all periodic scales contribute to the scattering pattern, Bragg's law is likewise useful in the analysis of superlattices, which are characterized by a mean superlattice peak, according to the average lattice parameter of the superlattice, and a set of equally spaced satellite peaks. The position of such satellite peaks are determined by the superlattice period thickness (t), which following Bragg's law is given by [169]:

$$t = \frac{(n_1 - n_2)\lambda}{(\sin \theta_1 - \sin \theta_2)}. \quad (3.8)$$

Therefore, the XRD in a superlattice structure provide the period thickness and accumulated strain.

Essentially, the XRD system consists of an X-ray generator source (an X-ray tube); a holder on which samples under study are placed and where the incident X-rays strike and diffract; and a detector, usually a Geiger counter or a Scintillation detector [170]. The Bragg-Brentano geometry allows the performance of θ - 2θ scans, as shown in Fig. 3.11, in which the position angle of the sample holder (θ) and the detector (2θ) with respect to the X-ray source continuously vary in order to retrieve the diffraction pattern. All the high-resolution XRD (HR-XRD) measurements shown in this thesis were conducted in the θ - 2θ mode at the ISOM facilities using Cu-K α 1 radiation (1.54056Å) in a Panalytical X'Pert Pro system

equipped with a Ge(220) hybrid monochromator. θ - 2θ scans were always performed around the (004) GaAs substrate reflection, characterized by a diffraction peak at 33.024° .

Fig. 3.11: Bragg-Brentano geometry for X-ray analysis.

3.3.4. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a scanning probe microscopy technique used to characterize material surfaces. Unlike X-STM, AFM is a non-destructive technique of characterization suitable for any kind of material, be it conducting or insulating. Fig. 3.12 shows a basic schematic of the AFM components and operation. The scanning probe consists of a cantilever, supported by a piezoelectric, with a sharp tip at its end. During the scan a laser beam strikes on the tip and is reflected towards a 4-quadrant sensor detecting the movement of the tip, which will allow the three-dimensional image of the surface.

An AFM can operate in two different imaging modes: static operation mode (contact mode) and dynamic operation mode (tapping mode). In the contact mode, the tip scans in hard contact with the sample surface. This is useful for small, high-speed atomic resolution scans. In the tapping mode, the cantilever oscillates intermittently tapping the surface. This scan mode virtually eliminates lateral forces commonly present in contact mode, such as drag, reducing the possible damage during the scan and improving lateral resolution on soft samples. Although the lateral resolution of AFM is low (on the order of 10 nm), the vertical resolution can reach ~ 0.1 nm. This is of particular interest for a fast evaluation of surface QD heights.

Fig. 3.12: Schematic of the AFM components and operation.

All the AFM measurements shown in this thesis were carried out at the ISOM facilities using a Bruker Multimode AFM with Sb-doped Si tips performed in tapping mode. Fig. 3.13 shows a representative $1 \times 1 \mu\text{m}^2$ AFM scan of surface QDs grown in this work showing a systematically found QD density near $3 \cdot 10^{10} \text{ cm}^{-2}$.

Fig. 3.13: Plan-view (left) and three-dimensional (right) AFM image of a representative $1 \times 1 \mu\text{m}^2$ area of surface QDs with a resolution of 512×512 lines.

3.4. Device processing

Once the samples are optically and structurally characterized, the devices of interest are processed. In this thesis, different p-i-n junction structures were fabricated for LEDs/photodetectors, LDs and solar cells. The fabrication technique consists of optical lithography, deposition of metallic contacts and wet chemical etching in the case of LEDs and solar cell devices. For LDs, a similar processing is required, but for some additional steps such as mechanical thinning and cleavage.

Fig. 3.14 shows the steps of the processing procedure for LEDs/photodetectors and solar cells. First, samples are cleaned using acetone and methanol and, then, completely covered in a photoresist (b). A lithographic mask is used to define an array of isolated mesa-like devices, exposing the photoresist surrounding them to ultraviolet light, which is then developed (c). The devices are all defined by a circular surface with a 200 μm diameter, allowing for the processing of a large number of devices from the same wafer area in which the temperature gradient during growth is negligible, leading to statistically reliable results which could not be otherwise possible. The sample is immersed in an acidic solution $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{H}_3\text{PO}_4$ (8:1:1), so that the surface free from photoresist is etched at a rate ~ 600 nm/min until the n-doped substrate is exposed (d). After etching, the n-type metallic contacts are evaporated, covering the whole surface of the sample (e). The n-type contact consists of an 80 nm-thick AuGe layer followed by a 300 nm-thick Au layer. After the evaporation, the photoresist is removed by a lift-off step immersing the sample in acetone (f). Once the photoresist is completely removed, the contacts are annealed at 360 $^\circ\text{C}$ in an H_2/N_2 atmosphere for 1 minute to form the ohmic contact. A second lithography step is performed, in which photoresist is applied (g) and the p contacts are defined on top of the mesas with the application of ultraviolet light through a specific mask, developing the exposed photoresist (h). The p-type metallic contacts are evaporated, which consist of a 10 nm-thick layer of Au, followed by an 80 nm-thick AuZn layer and finally by a 300 nm-thick Au layer (i). The photoresist is removed again by a lift-off step and the sample is subjected to a new annealing treatment in order to form the ohmic contact (j). The final appearance of the device is as shown in (k). Once processed, some characterization techniques will require the samples to be mounted on a TO5 and the contacts bonded with Au.

Fig. 3.14: Schematic of the fabrication steps in the processing of LEDs and solar cells. (a) Original piece of wafer. (b) The sample after cleaning and spinning of the photoresist. (c) First lithography. (d) Wet chemical etching. (e) Evaporation of the n-type metal. (f) Lift-off of the photoresist and annealing of the contacts. (g) Spinning of the photoresist. (h) Second lithography. (i) Evaporation of the p-type metal. (j) Lift-off of the photoresist and annealing of the contacts. (k) Final top view appearance of a fabricated LED/photodetector.

Fig. 3.15: Schematic of the fabrication steps in the processing of a LD. (a) Original piece of wafer. (b) The sample after cleaning and spinning of the photoresist. (c) First lithography. (d) Evaporation of the p-type metal. (e) Lift-off of the photoresist and contact annealing. (f) Spinning of the photoresist. (g) Second lithography. (h) Wet chemical etching and lift-off of the photoresist. (i) Thinning of the back side. (j) Evaporation of the n-type contact at the back side and annealing. (k) Final top-view appearance of a fabricated LD.

Although LDs are processed following a similar procedure, after the first cleaning of the samples (Fig. 3.15), lithography is first realized for the p-type contact using the suitable mask. This mask is designed in order to define 15, 25, 50 and 100 μm -thick lasers. Once the p-type ohmic contact is formed, a second lithographic step is carried out, covering the con-

tacts with photoresist, in order to mesa-etch the devices until the n-doped substrate is exposed. At this point, the samples are mechanically thinned with grinding paper on the back side up to a thickness of 100 μm to aid in the cleavage of the mirrors and to enhance the heat extraction efficiency. After achieving the desired thickness, the back surface is smoothed with diamond compounds of decreasing grain size. The back side of the sample is then metallized with the n-type metallic contacts. The same metallic multilayer structures used in the fabrication of the LEDs are also employed at the p- and n-type contacts of the LDs, following the same annealing procedure. Finally, the crystal is cleaved with the desired cavity length along parallel planes, forming this way a mirror at either side of the set of cavities contained in the wafer strip [171]. The final appearance of the devices is as shown in step (k) of Fig. 3.15.

3.5. Device characterization

3.5.1. Current-voltage measurements (I-V)

Current-voltage (I-V) measurements are a fundamental characterization technique allowing the fast drawl of valuable information on the electrical properties of diode devices. The current through the diode as a function of the voltage is given by the diode equation, which can be written as [140]

$$I_{dark} = I_0(e^{qV/mk_B T} - 1), \quad (3.9)$$

where I_0 is the diode saturation current and m the so-called ideality factor of the device and whose value may vary with the applied voltage, being ultimately conditioned by the predominant mechanism affecting current through the diode. In real devices, parasitic resistances may be present. In that case, the diode equation is written as

$$I_{dark} = I_0 \left[\exp \left(\frac{q(V - IR_s)}{mk_B T} \right) - 1 \right] + \frac{V - IR_s}{R_{sh}}, \quad (3.10)$$

where R_s and R_{sh} are the series and shunt resistances, respectively. Besides, the I-V curves commonly show different dominant regimes as a function of the applied bias. For instance, Fig. 3.16 shows the dark I-V curve for a non-ideal diode presenting a transition from a dominant SRH mechanism ($m=2$) at low bias into a dominant diffusive regime ($m=1$). The presence of a significant series resistance appears relevant at higher bias and can be extracted from the slope of a linear fit to the voltage increment as a function of the injected current [172]. Instead, the presence of a significant R_{sh} would be identified in the I-V curve by a symmetry at low negative and positive voltages [173].

Fig. 3.16: Representative semi-log I-V characteristics of a real diode at forward bias. Dashed lines represent the dominant regimes at low and high voltage with $m=2$ and $m=1$, respectively. The deviation from the ideal region at higher positive voltage is due to the presence of a series resistance R_s .

In this thesis, dark I-V measurements were conducted at ISOM using a Keithley 230 voltage source and a Keithley 617 electrometer according to the setup represented in Fig. 3.17. Samples were mounted on a circular platform where contact was made using triaxial probe tip holders. The setup also allows for the performance of I-V measurements under monochromatic illumination, using light from a quartz halogen lamp, dispersed through a 0.34-m monochromator. After passing through a high-pass filter, the dispersed light was driven towards the device surface by a set of lenses and mirrors. The diode is then placed under the light beam using the circular platform micropositioner. The impact of light on the I-V curve will be described in more detail in Section 3.5.5.

Fig. 3.17: Schematic of the setup used for dark and monochromatic light I-V measurements.

3.5.2. Electroluminescence (EL) spectroscopy

Electroluminescence (EL) spectroscopy consists of measuring the photons spontaneously emitted by the recombination of electron-hole pairs generated by the injection of current into the device. The same setup devoted to PL measurements and described in Section 3.2 is also used for EL measurements, with the exception that no laser is used for excitation. Instead, the devices are mounted and microbonded on a TO-5 package, so that current is injected into the device using a power source without the need for probe tips. Holes and electrons are injected through the p and n sides of the diode, respectively, and captured by the active layer, where they can eventually recombine radiatively. Like PL, EL allows evaluating the optical properties, in this case of processed devices.

The dependence of the integrated emission on the injected current can be assessed by collecting all the emitted light with a large area photodetector placed face-to-face to the facet of the device, as shown in Fig. 3.18. A PbS thermoelectrically cooled photodetector is used, whose spectral response is virtually flat in the range of wavelengths of interest. The signal from the detector is finally amplified by a lock-in amplifier, from which the external quantum efficiency of the device can be estimated.

Fig. 3.18: Schematic of the experimental setup used for measuring the LED-emitted power versus injected current.

In this thesis, continuous-wave injection current from a Keithley 230 source was used for low current densities, while for high current densities pulsed-wave injection from an ILX Lightwave LDP-3811 source was used, with a pulse width of 1 μ s and an 0.1% duty cycle.

3.5.3. Photocurrent (PC) spectroscopy

This technique allows measuring the current generated by the absorption of incident light. Once generated, electrons and holes are driven by the built-in field, under short-circuit conditions, towards the metallic contacts, so that the spectroscopic photoresponse can be measured by illuminating the sample with monochromatic light over a certain range of energies. The spectral responsivity of the sample is given by

$$R_\lambda = \frac{I_\lambda}{P_\lambda}, \quad (3.11)$$

where I_λ is the spectral photogenerated current and P_λ the spectral power of the light source. The external quantum efficiency is

$$EQE = R_\lambda \frac{h\nu}{q}, \quad (3.12)$$

where h is Planck's constant, ν is the frequency of the photon and q is the electron charge.

PC spectroscopy is useful to directly determine the effective gap. In addition, while it is complicated to observe EL emission above the lower effective band gap, unless the injected current saturates the lower energy states, spectroscopic PC allows identifying the absorption edge corresponding to every kind of structures within the intrinsic region of the device with absorbing energy levels within the measured range. Hence, the photogenerated current from QDs (ground and possibly excited states), CLs and the host GaAs will be identified through this technique.

PC measurements were carried out using the setup shown in Fig. 3.17 for I-V measurements. This setup also allows us to perform PC measurements under a certain applied bias in order to evaluate the dependence of the collection efficiency on the applied bias as a function of the region in which photons are absorbed.

3.5.4. Laser diodes (LDs): Figures of merit

3.5.4.1. LD emission spectrum

The analysis of LDs was first carried out by measuring the amplified spontaneous emission (ASE), below threshold, and lasing spectra. Such measurements will allow the determination of the lasing wavelength and, in the case of QDs, will tell us whether lasing occurs from the ground state or from excited states. The RT emission spectra of LDs were measured

with the help of an optical spectrum analyzer (OSA) in a setup like that shown in Fig. 3.19. Lasers are mounted onto a copper holder heat sink placed on a Peltier that allows controlling the temperature. Current is injected from a current source using a set of two tips, for a more homogeneous injection, and the optical emission is focused by means of a microscope objective onto a fiber coupler, previously aligned, and driven to the OSA by a multimode optical fiber. This fast system allows achieving optical spectra in a few seconds.

Fig. 3.19: Schematic of the setup for measuring LD spectra.

All RT amplified spontaneous emission (ASE) and lasing spectra measurements were conducted at the ISOM facilities using an ILX Lightwave LDP-3811 power source under pulsed conditions with a pulse width of 1 μ s and a 0.1% duty cycle.

3.5.4.2. Optical power-current characteristics

The optical power emitted as a function of the injected current is essential to evaluate the performance of a laser. A typical power-current density (P-J) curve of a LD is shown in Fig. 3.20 from which the threshold current density J_{th} is directly obtained as the intersection of the linear fit of the curve above threshold with the abscissa. In addition, the differential quantum efficiency η_d can be determined from the slope in the lasing region:

$$\eta_d = \frac{dP}{dJ}, \quad (3.13)$$

where P is the optical power and J the current density, taken above threshold.

Fig. 3.20: Typical P-J curve of a LD. Above J_{th} the spontaneous emission remains constant and the stimulated emission increases linearly with current density.

In addition, the dependence of J_{th} on temperature characterizes the thermal stability of the LD. This dependence can be approximated by the expression [174]:

$$J_{th} = J_0 e^{T/T_0}, \quad (3.14)$$

where T_0 is the characteristic temperature, in Kelvin, of the laser. The values for J_{th} drawn from the measurement of P-J curves at different temperatures are used to determine T_0 by a linear fit of $\ln(J_{th})$ versus temperature. Small T_0 values indicate a higher sensitivity of J_{th} with temperature so that high values for T_0 are desired.

The P-J measurements are conducted using the setup represented in Fig. 3.21. The LD is mounted onto a copper holder heat sink placed on a Peltier, which is used to vary the sample temperature within a certain range. The power source injects, through a pair of probe tips, the current into the LD, whose emission is now collected by a broad-area InGaAs photodetector placed face-to-face to the laser facet. Since pulsed current is usually injected in such measurements, the signal from the detector is recorded with a box-car averager. The transistor-transistor logic trigger signal of the current source is used as a reference for both the box-car and a control-oscilloscope. The oscilloscope is used to monitor the injected current pulse in order to ensure a square-like pulse.

Fig. 3.21: Schematic of the experimental setup for measuring the P-J curve of a LD.

All the P-J curves were measured at the ISOM facilities using an ILX Lightwave LDP-3811 power source under pulsed conditions with a pulse width of $1 \mu\text{s}$ and a 0.1% duty cycle. Measurements were carried out ranging the sample temperature from 10°C , just above the dew point to avoid condensation of water on the device, up to 40°C .

3.5.5. Solar cells

3.5.5.1. Current-voltage characteristics under air mass 1.5 direct radiation (AM1.5D)

The American Society for Testing and Materials (ASTM) defines the standard E490 Air Mass Zero extraterrestrial solar spectral irradiance (AM0) [175], shown in Fig. 3.22 (a), with an integral value of 1366.1 Wm^{-2} , as a reference spectrum for use by the aerospace community. For terrestrial solar-related measurements, ASTM defines the Air Mass 1.5 Global total spectral irradiance (AM1.5G) and, for concentrator cells and systems, the Air Mass 1.5 Direct normal spectral irradiance (AM1.5D) [176], which are, instead, derived from the extraterrestrial spectral irradiance reported by Gueymard et al. (1347.9 Wm^{-2} total integrated irradiance) [177] (see Fig. 3.22 (a)).

Fig. 3.22: (a) shows the standards ASTM AM1.5G and AM1.5D spectra, together with the standard ASTM AM0. (b) A solar zenith angle of 48.19° is considered in the standard AM1.5 solar irradiation.

The ASTM AM1.5G terrestrial solar spectrum (ASTM G173) represents the standard primary accepted by the international community for evaluating spectrally selective photovoltaic materials. This terrestrial solar spectrum is obtained by a software treatment of the extraterrestrial spectral irradiance using the average atmospheric conditions over a period of one year for the contiguous states of the United States of America [178] with an absolute air mass of 1.5. This value corresponds to a solar zenith angle of 48.19° (Fig. 3.22 (b)), which approximately represents the overall yearly average atmosphere thickness through which the solar spectrum travels for mid-latitudes. The standard AM1.5G finally corresponds to the normalization of the resulting spectrum to the representative average latitude of the conterminous United States (37°), so that the total integrated irradiance is 1000.4 Wm^{-2} . Diffusive light from Rayleigh scattering in the atmosphere and the albedo, reflected by the surroundings, is excluded in AM1.5D, which only considers radiation coming from a 5.8° aperture angle of the sun disc (900.1 Wm^{-2} total integrated irradiance). This is the standard used for solar devices that include optics, as it is the case of concentration photovoltaic devices, since the diffuse component of the solar radiation cannot be focused on the device.

Under light illumination, the overall current passing through the solar cell can be approximated as the sum of the photogenerated current (I_L) and the dark current (I_{dark}), which, according to the convention in photovoltaics that the photocurrent is positive, is written

$$I(V) = I_L - I_{dark}(V). \quad (3.15)$$

This approximation is graphically represented in Fig. 3.23 (a). Under light illumination, the cell operates within the range of bias from 0 to the open-circuit voltage (V_{oc})¹ delivering a power given by

$$P = IV \quad (3.16)$$

and represented in Fig. 3.23 (b) as a red line. The operating power reaches the maximum value (P_{max}) at a certain voltage V_{mp} , below the V_{oc} , corresponding to a current I_{mp} below the short-circuit current (I_{sc})². V_{mp} is therefore the operating power of the solar cell. The fill factor (FF) is a parameter defined as

$$FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}, \quad (3.17)$$

graphically illustrated as the area of the largest rectangle fitting in the I-V curve (light gray square in Fig. 3.23 (b)), giving a measure of its “squareness”.

The efficiency η of the solar cell is defined as the fraction of the incident light power (P_{in}) converted by the solar cell at the operating point and can be described by the FF in conjunction with V_{oc} and I_{sc} as

$$\eta = \frac{V_{mp}I_{mp}}{P_{in}} = \frac{V_{oc}I_{sc}FF}{P_{in}}. \quad (3.18)$$

High I_{sc} , V_{oc} and FF are therefore desired for improved conversion efficiencies.

¹ V_{oc} is the maximum voltage available from a solar cell, which occurs at zero current. According to the diode equation and neglecting the presence of parasitic resistances, V_{oc} can be expressed as $V_{oc} = (mk_B T/q) \cdot \ln(I_L/I_0 + 1)$. On one hand, V_{oc} will be influenced by the saturation current I_0 , decreasing with it. On the other hand, V_{oc} will increase with the ideality factor, which directly depends on the sort of recombination mechanisms taking place in the solar cell.

² I_{sc} is the current through the solar cell when this is short-circuited and voltage across it is therefore zero. In case of complete carrier collection efficiency under photovoltaic conditions, I_{sc} can be assumed to be approximately I_L .

Fig. 3.23: (a) Diode I-V characteristics under dark (green) and light illumination (black) conditions. The photogenerated current I_L is shown as a blue horizontal line. (b) IV curve under light illumination (black) and power-voltage (red) characteristics of a diode solar cell. The FF is defined as the fraction of the dark gray square, defined by $V_{oc} \times I_{sc}$, covered by the light gray square, defined by $V_{mp} \times I_{mp}$.

All the solar cell devices presented in this thesis were characterized under AM1.5D conditions at Instituto de Energía Solar (IES), Universidad Politécnica de Madrid (Spain). The used light source is a solar simulator equipped with a 150 W Xenon Lamp and an AM1.5D filter combination (Newport). The total light intensity was calibrated to 900 Wm^{-2} using a GaAs reference cell and photocurrent density-voltage (J-V) measurements were conducted using a Keithley 2400 source meter.

3.5.5.2. Current-voltage characteristics under light concentration

Light concentration is in some cases appropriate to improve the efficiency of a solar cell. Assuming an incident flux of light increased by a factor X , the photogenerated current under concentration in equation 3.15 will be given by:

$$I_L(X) = XI_L, \quad (3.19)$$

so that

$$I(V) = XI_L - I_{dark}(V) \approx XI_L - I_0(e^{qV/mk_B T} - 1). \quad (3.20)$$

The net current increases with the concentration factor X , thereby increasing the V_{oc} , which following equation 3.20 becomes:

$$V_{oc}(X) = \frac{mk_B T}{q} \ln \left(\frac{XI_L}{I_0} + 1 \right) = V_{oc}(1) + \frac{mk_B T}{q} \ln(X). \quad (3.21)$$

Hence, the V_{oc} increases logarithmically with light concentration from its value under unconcentrated light ($V_{oc}(1)$) and linearly with the ideality factor m , leading to an increase of the solar cell efficiency if FF remains the same.

Since, regardless of the excitation energy, every generated electron-hole pair will be rapidly thermalized before collection, the use of monochromatic light from a laser can be used to readily analyze the impact of light concentration on the V_{oc} . Such measurements represent a reliable way to analyze the impact of light concentration as a function of the device structure, despite the possible introduction of contact resistance, with an expectedly similar behavior as in concentrated AM1.5D conditions. Indeed, even in the event that significant resistive effects are present, they exert no effect on the V_{oc} , in which conditions no current flows through the diode.

In this thesis, the impact of light concentration is analyzed by using light from a solid-state power-tunable LD emitting at 781 nm according to the setup in Fig. 3.24. The light power intensity of the laser beam is additionally controlled with the help of an attenuating filter placed at the laser output and calibrated with a Liconix 45PM laser power meter. A set of lenses and mirrors is used to focus the laser beam onto the sample, which is connected to a semiconductor parameter analyzer in order to carry out I-V measurements under different light power intensities.

Fig. 3.24: Schematic of the setup used for I-V measurements under light concentration.

Part I: GaAs/InAs/GaAs quantum dots

Most efforts on controlling InAs QD properties have commonly been focused on the growth conditions leading to a good understanding of the QD growth mechanism. The growth rate [63–66] and the growth temperature [67], as well as the time interval between the interruption of the QD growth and the capping process [68] play an essential role in determining the morphology of InAs QDs after their initial formation. Less attention has been paid to the capping process, which can significantly affect the final QD properties. Indeed, capping with GaAs leads to a considerable dissolution of QDs, significantly altering their morphology and, therefore, their optoelectronic properties [69,72–77]. This means that, however accurate the QD growth conditions are, the QD size and shape will ultimately be affected by the capping process, which is necessary for almost any device application. The chapter in Part I explores a straightforward approach to control the QD size during the over-growth process without the need to resort to complex strain-engineering strategies.

4 Structural and optical tunability of GaAs/InAs/GaAs quantum dots through the capping rate

4.1. Introduction

Since the experimental realization of semiconductor QDs and the observation of their unique properties, increasing efforts have been made in order to take advantage of such structures for real applications. QDs, and more in particular InAs QDs, have aroused many expectations not only for the development of more efficient optoelectronic devices, as described in Section 1.1, but also as a key element in quantum information applications [179–181]. However, the achievement of small fine structure splitting energies in order to produce entangled photon pairs is highly conditioned by strict geometrical requirements [182]. Indeed, geometry and composition determine the properties of QDs [61,62], strongly affecting the performance of lasers, solar cells or any other optoelectronic devices based on QDs. Strain engineering by the use of alternative capping materials has been a commonly employed strategy in order to prevent QDs from dissolution during overgrowth offering a certain degree of control over the QD size and shape [42,110,114,116–118,121,125–128,183,184]. This occurs, however, at the expense of significant and inevitable additional electronic or structural modifications which might not be desirable in some cases. For instance, although the use of GaAsSb CLs strongly limits the QD dissolution, a high Sb content entails a transition of the band alignment into a type-II structure [108]. A band alignment transition may also be induced by the introduction of N into the CL [109], while the use of InGaAs may even induce a QD shape evolution into columnar QDs [185].

In this chapter, we propose a very straightforward way to control the size and, therefore, the optoelectronic properties of standard GaAs/InAs/GaAs QDs by simply tuning the capping rate. This will modify the intermixing process, additionally affecting the final WL structure, whose impact on the performance of optoelectronic devices is recently gaining an increasing interest [186–189]. The impact of the capping rate on the properties of GaAs/InAs/GaAs QDs and WLs are both analyzed in this work.

4.2. Sample description

A series of three samples containing a single QD layer was grown for PL studies. In all these samples, 2.8 MLs of InAs were deposited at 450 °C and 0.04 MLs⁻¹ on a 500 nm-thick intrinsic GaAs buffer layer grown at 580 °C. The QD layer was subsequently capped by a 30 ML-thick low-temperature (LT) GaAs layer grown at 470 °C at 0.5, 1.0, and 2.0 MLs⁻¹ in samples S₀, S₁, and S₂, respectively, followed by a 250 nm-thick GaAs layer grown at 580 °C and 1.0 MLs⁻¹. An additional sample for TEM and X-STM measurements, labeled as S₃, was grown containing three QD layers equivalent to those of S₀, S₁, and S₂ (L₀, L₁, and L₂

QD layers, respectively), separated from each other by a 50 nm-thick GaAs spacer grown at 580 °C (Fig. 4.1). Finally, a 200 nm-thick intrinsic GaAs layer was deposited, on top of which a fourth layer of uncapped QDs was grown for reference (L_s).

Fig. 4.1: Sketch of sample S_3 containing three QD layers capped at 0.5 (L_0), 1.0 (L_1), and 2.0 MLs^{-1} (L_2), and a surface uncapped QD layer (L_s).

4.3. Results and discussion

Fig. 4.2 (a) shows the 15 K PL spectra of samples S_0 , S_1 , and S_2 , together with the spectrum obtained from the sample containing the equivalent QD layers (S_3). A red-shift of the PL peak energy is found with an increase of the capping rate: from 1181 eV, capping at 0.5 MLs^{-1} (S_0), to 1118 eV, capping at 1.0 MLs^{-1} (S_1), and to 1096 eV, capping at 2 MLs^{-1} (S_2). Three peaks at similar energies are also observed in the PL from the multi-QD-layer sample (S_3), corresponding to the emission from the three QD layers equivalent to those of S_0 , S_1 , and S_2 . The apparent shoulder at ~ 1.2 eV suggesting the presence of a fourth peak at higher energies is only due to a drop in the system responsivity, which also gives rise to a notch-like shape in the PL curve of S_0 . The shift of the PL peak to lower energies is indicative of a QD morphology evolution when the capping rate is increased. In addition to the red-shift

of the PL peak energy, improved linewidth and integrated intensity are achieved with a high capping rate (Fig. 4.2 (b)). The FWHM is reduced from 61 to 42 meV when the capping rate is increased from 0.5 (S_0) to 2 MLs^{-1} (S_2), whereas the integrated intensity is almost doubled.

Fig. 4.2: (a) 15 K PL spectra of samples S_0 , S_1 , S_2 , and S_3 and (b) the integrated intensity and FWHM as a function of the capping rate. Lines are guide to the eye.

Statistical results on the QD size and shape can be drawn from TEM measurements. Fig. 4.3 (a) shows g002 dark-field X-TEM images taken on the [110] pole axis containing views of the layers L_0 , L_1 , and L_2 in sample S_3 , along with a high-resolution view of the surface QD layer, L_s . A number of more than 60 QDs from each layer was measured, finding no significant difference for the base diameter, which is within the range of 21.0 ± 0.5 nm in all the samples. As for the QD height distribution, represented in Fig. 4.3 (b), average values of 3.72 ± 0.14 , 3.96 ± 0.16 , and 4.41 ± 0.22 nm, were found for the L_0 , L_1 , and L_2 layers, respectively, while the height of the surface unburied QDs was found to be 4.38 ± 0.22 nm, closely matching that of L_2 . A change in the QD height is therefore confirmed to be the main factor affecting the PL properties. A complete preservation of the QD height and size dispersion is achieved capping at 2 MLs^{-1} , while lower capping rates lead to a reduction of the QD height and its dispersion by means of a QD shape evolution from a full pyramidal shape to a truncated or lens-shaped QD. Hence, high capping rates preserve not only the QD height but also its geometry. For the used growth temperature, it can be assumed that bulk migration is minimal, so that the strong dependence of the QD size and shape on the growth rate of the CL must be kinetically governed by slow surface intermixing processes with characteristic times in the range of ~ 1 s. Thus, low capping rates would favor a thermodynamically controlled regime, inducing an In-Ga intermixing at the CL growth front, eroding the pyramidal QD apex and increasing the roundness of the side facets, while keeping the QD base diameter [190,191]. Contrarily an increase of the capping rate will kinetically restrain surface intermixing, facilitating the preservation of metastable QD structures and significantly increasing

the aspect ratio. Remarkably, this is achieved even in a system with a high lattice mismatch between InAs QDs and GaAs CL ($\Delta a \sim 7\%$) without the use of strain-engineering strategies [117].

Fig. 4.3: (a) g200 dark-field X-TEM images of representative areas of L_0 , L_1 , and L_2 in sample S_3 , along with a high-resolution view of the surface QD layer, L_s . (b) QD height distributions measured by TEM for layers L_0 , L_1 , L_2 and L_s plotted in a box chart, together with the corresponding histograms. The box is defined by the 25th and 75th percentiles, where the horizontal line and the solid square in the center of the box are the median and the mean of each population, respectively. The lines extending vertically from the boxes (whiskers) are determined by the 5th and 95th percentiles.

As observed in Fig. 4.4 (a), the height of capped QDs follows a linear dependence on the capping rate and their complete preservation is achieved at capping rates as of $\sim 2.0 \text{ MLs}^{-1}$. The higher preservation of the QD height at faster capping rates leads to a red-shift of the PL peak energy (Fig. 4.4 (b)). Moreover, the PL peak energy follows the expected trend as a function of the average QD height in each layer [107]. Besides the strong impact on the ground state transition, more localized electron and hole wavefunctions in k space are expected for higher QD height, resulting in an enhanced ground state optical matrix element in the measured range and independently of the QD shape [192]. This factor along with a stronger carrier confinement [193] are in agreement with the enhanced PL integrated intensity with the QD height. On the other side, the TEM measurements show that the size dispersion observed in the uncovered QDs is preserved for QDs capped at a high growth rate, while it narrows down when lower capping rates are used (see Fig. 4.3 (b)). This is, in principle, in disagreement with the PL FWHM evolution observed in Fig. 4.2 (b), since a broader QD size distribution is intuitively expected to yield a broader PL linewidth. Nevertheless, a narrower dispersion of the effective band gap is found in Fig. 4.4 (b) for the higher QDs (capped at higher growth rates), despite the higher size fluctuations within the ensemble. This is a consequence of the stronger dependence of the band gap energy on the QD height

for smaller QDs. Hence, this factor seems to be governing the PL emission shape counterbalancing the broader QD size distribution and giving rise to the narrower emission linewidth for the QD layers capped at higher rates.

Fig. 4.4: (a) QD height as a function of the capping rate in the three different layers studied by TEM. The black dashed line represents the uncapped QD height, indicating a completely suppressed decomposition process. The blue dashed line is a linear fit to the QD heights at L_0 , L_1 , and L_2 . The two different background colors indicate two different regimes, whereby the QD height is first linearly increased with the capping rate and then completely preserved for capping rates above $\sim 2 \text{ MLs}^{-1}$. (b) 15 K PL peak energy as a function of the QD height showing the stronger dependence on size dispersion for smaller QD heights.

For further understanding on the impact of the capping rate, sample S_3 was analyzed by X-STM. In this technique, the cleaved surface is atomically resolved providing additional information on the QDs as well as on the WL. Measurements in constant current mode are performed under high negative bias conditions ($\sim 3 \text{ V}$) strongly suppressing the electronic contrast, so that mainly topographic information is drawn through this imaging mode [166]. Fig. 4.5 shows representative topography images of the nanostructures found in L_2 (a), L_1 (b), and L_0 (c-e). The bright horizontal lines are the top zig-zag rows of the cleaved surface, which are separated by one atomic bilayer and define the resolution along the growth direction in our measurements (0.56 nm). Indium atoms in the group-V sublattice give rise to brighter spots. The pyramidal shape is distinguished in the highest QDs from L_2 (capped at 2 MLs^{-1}) showing steeper facets (Fig. 4.5 (a)). This shape is not observed in L_1 and L_0 QD layers (Fig. 4.5 (b) and (c), respectively), where the QD apex and facets are more dissolved and the QDs have evolved into lens-shaped QDs [184]. Some crater-like structures were also found in layer L_0 (lowest capping rate) (Fig. 4.5 (d)), which represent the first stage in the evolution of the QDs into quantum rings (QRs) (Fig. 4.5 (e)) [72,194,195]. InAs QRs are commonly fabricated starting from partially covered InAs QDs and applying a brief post-

growth annealing (<1 min). Annealing at 470°C , the temperature used for the capping of QDs in our sample, has been found to be sufficient to obtain well defined QRs [196]. The capping rate at this QD layer is so low (~ 8 nm/min) that the outward migration of In atoms from the QD center region becomes a relevant process, giving rise to the formation of some QRs from the lens-shaped QDs. The typical QR shape is perfectly identified on the current image in Fig. 4.5 (f), showing the outline of the nanostructure typically found in QRs [195]. This indicates that the QR morphology is closer to the thermodynamic equilibrium. The structure evolution is kinetically controlled during the overgrowth, so that adjusting the capping rate allows tuning the final metastable structure, from completely preserved pyramidal QDs, to partially dissolved lens-shaped QDs, to QRs. This morphological evolution is likely driven towards a homogeneous quantum well structure as the thermodynamic equilibrium state [73,190].

Fig. 4.5: X-STM topography image of the nanostructures found at L_2 (a), L_1 (b), and L_0 (c-e). (f) Current image mode of (e), showing the outline of the nanostructure typically found in QRs.

The WL in each QD layer was also analyzed by X-STM. Fig. 4.6 shows representative topography images of the WL in L_0 (a), L_1 (b), and L_2 (c). The topographic contrast is induced by the outward relaxation of the cleaved surface due to the compressive strain stemming from the WL. Our analyses are performed over an extended region along the WLs, covering a total length between 200 and 400 nm for each WL. The considered areas are chosen to be sufficiently distant from any QD in order to exclude their effects on the WL in the neighborhood of the QD. The results clearly show a reduction of the WL thickness with increasing capping rates. In order to quantitatively assess the differences between the WLs, the outward relaxation profile of each layer was averaged over the whole imaged area and this averaged profile is depicted in Fig. 4.6 (d). The comparison between the areas under the outward relaxation profiles (i.e. the integral of the contrast profiles) provides a direct information on the difference in the amount of In present in each WL [160,166]. The average areas under the profiles, normalized with respect to the area under the L_0 profile, are depicted

in the inset of Fig. 4.6 (d). A reduction of 37% in the outward relaxation area is found when the capping rate is increased from 0.5 to 2 MLs⁻¹, pointing out the significant reduction in the content of In in the WL. This difference can be understood as another result of the decreased dissolution of the QDs when a high capping rate is used: for low capping rates the strain can be relieved through the flattening of the QD pyramidal shape, which leads to an In segregation from the QD back to the WL. Contrarily, when the capping rate is high this process is kinetically suppressed by a kinetic effect, and the In concentration outside the QDs will remain lower [190]. The occurrence of this process during capping is also predicted by kinetic Monte-Carlo simulations [116], where the redistribution of In atoms from the QD tops to the areas in-between them gives rise to flat top facets at low capping rates [69,116,190]. Hence, capping at high rates not only allows the preservation of the QD height, but also reduces, to a large extent, the WL thickness by the inhibition of In atoms redistribution. Therefore, this approach provides an additional degree of freedom to improve carrier transport in QD photodetectors [187] and solar cells [189] or to avoid the V_{oc} drop induced by the WL [186,188] among other possible benefits.

Fig. 4.6: Representative X-STM topography images of the WL at L_0 (a), L_1 (b), and L_2 (c). (b) Relaxation profiles of the WLs averaged along the overall measured WL length at L_0 , L_1 , and L_2 . The inset shows the average relaxation area as a function of the capping rate, normalized to that of L_0 (lowest capping rate). The black dashed line is a guide to the eye.

4.4. Conclusions

In conclusion, we have shown a very straightforward approach to control the final structural properties of InAs QDs capped with GaAs. An improved preservation of the QD height and shape is found by merely increasing the capping rate, leading to the complete QD preservation and suppressed decomposition for rates above ~ 2.0 MLs⁻¹. This only parameter allows an easy tunability of the structural QD properties and, therefore, of the ground state

energy without the need for a different capping material or an annealing process. This approach could also give an additional degree of freedom in the search for the demanding geometrical requirements of QDs leading to lower exciton fine-structure splitting energies for new QD applications in quantum information. On the other side, the higher preservation of the QD with the capping rate is found to be due to reduced surface In-Ga intermixing at the growth front. This limits the diffusion of In atoms from the QDs to the regions in-between them, giving rise to thinner WLs. This approach could therefore be also beneficial in optoelectronic applications in which the WL is known to affect the device performance, such as QD infrared photodetectors or QD solar cells. Most probably, this simple approach could be transferred to any other QD structure based on different materials, which could also take advantage of an easy way to control the QD degree of dissolution.

Part II: GaAsSb/InAs/GaAs quantum dots

The use of an alternative capping material, instead of directly capping with GaAs, allows a large tunability of the optical properties of InAs QDs. In particular, the use of GaAsSb strain-reducing CLs has been found to extend QD emission towards the optical-fiber telecommunication wavelengths [41,42,106,121]. The addition of Sb raises almost exclusively the valence band of the CL [197], so that such long emission wavelengths are achieved switching the QD-CL band alignment from a type I to a type II for an Sb content around 16% [42] (See Fig. 2.8). In addition, improved luminescence properties are obtained for moderate Sb contents, for which the type-I alignment remains [108]. This is in part ascribed to the simultaneous preservation of the QD height through the application of such CLs [113,162], which is believed to enhance the carrier confinement. These properties make GaAsSb/InAs/GaAs QDs promising not only for QD lasers, but also for QD solar cells. Since the MBE growth of these QDs was previously optimized at ISOM, efforts have been focused on their application to such kind of devices. Chapters 5 and 6 in Part II will deal with both LDs and solar cells, respectively, focusing on the impact of the Sb content and the Sb-induced band alignments on the performance of such devices.

5 GaAsSb/InAs/GaAs quantum dot lasers

5.1. Introduction

Despite the latest advances in the understanding of GaAsSb-capped InAs/GaAs QDs, only a few reports have demonstrated QD lasers in this system [41,198]. Moreover, the role of the Sb content and the transition from a type-I to a type-II band alignment in QD lasers has not been addressed as yet. Indeed, there are almost no reports on any kind of type-II QD lasers [137,138]. Nevertheless, type-II QD lasers might present advantages such as wavelength and gain tunability [137–139] as well as an inhibition of spontaneous emission and Auger recombination. This could result in a reduced J_{th} , as it has been predicted for type-II QW lasers [139,199]. Hence, the goal of this chapter will be to analyze the impact of the Sb content and the band alignment on the performance of GaAsSb-capped InAs/GaAs QD lasers. Samples presenting type-I and type-II band alignments will be designed, grown and processed as broad-area edge-emitting lasers. The study will also encompass lasers with different cavity lengths, since this factor has a significant impact on J_{th} [174].

5.2. Sample description

The active region of the analyzed series of samples consists of five InAs QD layers grown at 450 °C by depositing 2.8 MLs at ~ 0.04 ML/s, capped with a 5 nm-thick GaAsSb layer at 1 MLs⁻¹. The CL growth temperature, known to be a critical factor affecting the final QD-GaAsSb CL configuration, was set to 470 °C in order to avoid material migration from the CL at the QD top region, taking place for higher CL growth temperatures [113]. Immediately after the CL, a 10 ML-thick LT GaAs layer was grown at the same temperature in order to avoid Sb desorption. Three samples with 0, 8 and 18% Sb were grown, from now on labeled Sb₀, Sb₈ and Sb₁₈, respectively. The capped QD layers were separated among themselves by 50 nm of GaAs grown at 580 °C and the whole active region was embedded in the middle of a 300 nm-thick undoped GaAs layer. 2 μ m-thick Al_{0.3}Ga_{0.7}As cladding layers (1.85 μ m doped) grown at 610 °C were used for light confinement. The LD structure was grown on a 350 nm-thick n⁺-GaAs buffer layer and ended with a 250 nm-thick p⁺-GaAs contact layer. The sketch of the complete LD epitaxial structure is shown in Fig. 5.1. Broad-area edge emitting lasers with 15 μ m-wide stripes were fabricated as described in Section 3.4, with as-cleaved facets on both sides and cavity lengths (L_c) of 1000 and 1300 μ m.

Fig. 5.1: Sketch of the LDs containing five stacked InAs QD layers capped with a thin GaAs(Sb) CL.

5.3. Results and discussion

5.3.1. Spectral analysis

Fig. 5.2 shows the 15 K PL spectra of the three unprocessed samples. As expected, the PL wavelength is red-shifted as the Sb content is increased in the CL, and the PL intensity is enhanced for moderate Sb contents, in agreement with previous studies [108,200]. The

transition from a type-I band alignment in Sb_0 and Sb_8 to a type-II band alignment in Sb_{18} was confirmed through the analysis of the dependence of the emission peak energy on the excitation power (inset of Fig. 5.2). A clear blue-shift is observed in sample Sb_{18} , with a linear dependence on the third root of the excitation power, as expected for a type-II system where the photoexcited carriers are spatially separated (see Section 3.2) [158]. In contrast, the peak energy of samples Sb_0 and Sb_8 is independent of the excitation power. Thus, sample Sb_8 presents a type-I band alignment, while sample Sb_{18} shows a type-II alignment with the hole wavefunction localized outside the QD, in the CL, as shown in Section 2.5 [106].

Fig. 5.2: 15 K PL spectra for samples Sb_0 , Sb_8 , and Sb_{18} . The inset shows the peak energy as a function of the third root of the excitation power for each sample.

Power-current (P-I) curves and the lasing spectra of the three QD LDs with a cavity length $L_c=1300$ μm are shown in Fig. 5.3. Lasing wavelengths of 1072, 1160 and 1164 nm are observed at RT for samples Sb_0 , Sb_8 and Sb_{18} , respectively. In addition to the wavelength shift with the Sb content, J_{th} is seen to be highly dependent on the Sb content, effect that will be addressed later. In order to identify the origin of the laser emission, the below-threshold ASE and the RT PL were measured in all devices (Fig. 5.4). In the case of samples Sb_0 and Sb_8 , it is clear that the ground state observed in the PL and ASE is saturated and laser emission originates in the first excited states. In the case of Sb_{18} , the main peak of the ASE matches the RT PL, and is hardly shifted from the low-temperature PL peak. This effect, added to the fact that the RT PL shows a shoulder at longer wavelengths, suggests that the observed main peak does not correspond to the ground state transition. Indeed, the ASE spectrum measured at a much lower current density shows two low energy shoulders with

peak wavelengths of 1292 and 1335 nm (obtained from a three-peak Lorentzian fit to the spectra, see Fig. 5.4 (d)). Moreover, this lower energy peak blue-shifts with increasing carrier density as the third root of the injected current, as shown in the inset of Fig. 5.4 (d). The higher energy peak at 1247 nm, which is the main peak in the RT PL and higher current ASE in Fig. 5.4 (c), does not show any blue-shift suggesting that it is not a pure type-II state, in which the hole wavefunction is likely delocalized between the QD and CL region. The long wavelength weak shoulder should therefore correspond to the type-II ground state transition, which, contrary to what happens in the type-I samples, seems to be strongly inhibited in the ASE. Therefore, in sample Sb_{18} lasing is originated in the type-I-like third excited state (Fig. 5.4 (c)), giving rise to a much shorter wavelength than expected.

Fig. 5.3: P-I (per facet) curves for Sb_0 , Sb_8 , and Sb_{18} for $L_c=1300 \mu\text{m}$. The inset shows the laser spectra above threshold for the three QD LDs.

The inhibition of the ground and even first excited state spontaneous emission in the type-II QD LDs is indicative of a very long carrier lifetime, which can only compete with non-radiative recombination at very low temperatures at which non-radiative channels are negligible. Nevertheless, strong RT PL from the ground state is observed in similar type-II QD layers when they are not inserted in a p-n junction [106,108]. A possible explanation for such a ground state inhibition could therefore be the presence of the built-in electric field created by the p-n junction. To understand this effect, one has to account for the charge distribution in type-II QDs, where the maximum of the ground state hole probability density is located outside the QD, close to the QD-capping interface. This hole probability density maximum is split in two regions found at the base of the QD and aligned in the [110] direction (Fig. 2.8 (d)) [106,201]. Since the built-in electric field in the structure is oriented in the

growth direction, it will push the electrons downwards, deeper into the QDs, and the holes upwards towards the top GaAsSb/GaAs interface. This will strongly increase the spatial separation of their wavefunctions and the carrier lifetime and, therefore, will reduce the oscillator strength, resulting in the observed inhibition of the ground state transition [202]. In the type-I samples, on the contrary, the electric field could increase the wavefunction overlap, since the electrons are typically located towards the top of the QD and the holes towards the bottom [203]. A similar effect has been recently described for GaAs-capped InAs QDs inserted in a p-i-n junction [204]. The very large carrier lifetime induced by the interaction of the QD dipole with the built-in field could be an inherent impediment to achieve ground state lasing from these type-II systems, since it will also considerably reduce the gain [174]. Smaller QDs, thinner GaAsSb CLs and a thicker intrinsic region in the p-i-n structure (to reduce the electric field) would in principle reduce this effect.

Reaching longer wavelengths would require lasing from the ground state, or at least from lower excited states. To do so, several approaches may be pursued. First, the QD density is likely too low in these structures to achieve enough gain at the ground state, effect that could be overcome by increasing the number of QD layers. In addition, although ground state lasing could hardly be achievable in the type-II sample for the reasons already discussed, switching the lasing mode between different excited states is possible by modifying the cavity length (Fig. 5.4 (c)). Indeed, with a 1300 μm cavity length (Sb_{18a}) laser emission at the third excited state is obtained (at 1164 nm), whereas for a 1000 μm cavity length (Sb_{18b}) lasing proceeds via the fourth excited state (at 1078 nm, Fig. 5.4 (c)). This is a consequence of the reduced J_{th} for longer cavity lengths. Thus, it could be possible to obtain laser emission at lower excited states, i.e., longer wavelengths, by further lengthening the cavity of the laser.

Fig. 5.4: ASE spectra for different currents below threshold for Sb_0 (a), Sb_8 (b), and Sb_{18} (c) for a 1000 μm -long cavity. The RT PL spectra of the unprocessed samples and the normalized lasing spectra are also shown in all cases. In sample Sb_{18} two lasing spectra are shown for two cavity lengths: 1300 μm (Sb_{18a}) and 1000 μm (Sb_{18b}). (d) Measured ASE spectrum at very low injection current for sample Sb_{18a} , together with a three-peak Lorentzian fit. The inset shows the energy of the longer wavelength peak extracted from the Lorentzian fit as a function of the third root of the injected current, together with the resulting linear fit.

5.3.2. Threshold current and efficiency

In order to quantify the effect of the Sb content on J_{th} and η_d , several devices were measured from each of the three samples. Fig. 5.5 shows the average values in the three samples for 1000 μm -long QD LDs. One can observe that η_d is strongly improved as a result of adding Sb, increasing from 14% in the reference sample to 19% in the type-I QDLD (sample Sb_8). However, a decrease is obtained for Sb_{18} compared to the reference Sb_0 . On the other hand, there is a reduction by a factor of two in J_{th} in both type-I and type-II Sb-containing

QD LDs with respect to the reference Sb-free QD LD. Note that the J_{th} values obtained for our reference GaAs-capped InAs QDs are not as low as some previously reported [205,206]. This is probably due to problems with calibration of Al during the growth of the cladding layers, resulting in an unoptimized structure. Nevertheless, since the three samples were grown under the same conditions, this does not affect the comparative purpose of this work. The strong improvement provided by the presence of Sb becomes clear.

Fig. 5.5: J_{th} and η_d for lasers with $L_c=1000 \mu\text{m}$ as a function of the Sb content in the CL. Lines are guides to the eye.

The improvement of the lasing characteristics when Sb is present in the CL of the QD LDs could also be the results of increased carrier injection efficiency, as it has recently been suggested [106]. While both electrons and holes are mainly injected through the WL in GaAs-capped QDs and have a considerable probability of recombining there, the presence of the GaAsSb layer would lead to a separate and more efficient injection of carriers: electrons through the WL and holes through the GaAsSb layer, avoiding radiative recombination in the WL. In the case of the type-II QD LD, the inhibition of the spontaneous emission from the type-II states previously described would produce a reduction of the radiative component of J_{th} , contributing to a faster build-up of the gain (in the type-I-like excited states). Indeed, this effect has been theoretically predicted by Chow and Schneider in type-II QW lasers [139].

5.3.3. Characteristic temperature

The temperature behavior of the devices was also investigated. Fig. 5.6 shows the temperature dependence of the P-I curves for 1000 μm -long cavity QD LDs of the three samples.

The insets show the corresponding linear fit to $\ln(J_{th})$ versus temperature, from which characteristic temperatures of 42, 39 and 99 K are obtained for Sb_0 , Sb_8 and Sb_{18} , respectively. While there is no significant difference for sample Sb_8 compared to the reference Sb_0 , a very strong improvement in T_0 is found for sample Sb_{18} . Indeed, values of up to 130 K were found in this sample for QD LDs with a 1300 μm cavity length. This improvement in T_0 for the type-II QD LDs may be explained as follows. First, the increased QD height with the Sb content [108] would increase the barrier for electron overflow from the QD to the CL, which is typically one of the reasons for the increased dependence of J_{th} with temperature. Indeed, the improved thermal stability of the type-II QD LDs is likely related to that of the PL, which is much larger for the QDs capped with high Sb contents [106]. Second, in type-I samples the small valence band offset could favor hole escape from the QDs, yielding a lower T_0 . In contrast, in the type-II structures the holes are already confined in the CL, and thus raising the temperature would have a much smaller effect, yielding a high T_0 .

Fig. 5.6: Temperature dependence of the P-I (per facet) curves for samples Sb_0 (a), Sb_8 (b), and Sb_{18} (c). The inset of each Fig. shows a linear fit to $\ln(J_{th})$ versus temperature from which the respective T_0 is obtained. (d) Characteristic temperature T_0 as a function of the Sb content in the CL. Lines are guides to the eye.

5.4. Conclusions

In conclusion, the effect of modifying the amount of Sb in a series of GaAsSb/InAs/GaAs QD LDs was studied. The lasing wavelength red-shifts with the Sb content, but it is shorter than expected due to lasing from excited states. This could, in principle, be avoided by increasing the number of QD layers. This effect is particularly important in the type-II QD LDs, in which the ground state transition is inhibited in the ASE likely due to the presence of the junction built-in electric field. Despite this, J_{th} is strongly reduced by using a GaAsSb CL, whereas η_d is substantially improved for moderate Sb contents in the type-I band alignment region. Moreover, T_0 is more than doubled for high Sb contents in the type-II region.

6 GaAsSb/InAs/GaAs quantum dot solar cells

6.1. Introduction

The implementation of GaAsSb/InAs/GaAs QDs in photovoltaic devices will be the focus of this chapter. The application of thin CLs to QD solar cells has hardly been investigated thus far [207,208] for what the novel use of GaAsSb CLs could bring additional advantages. The ability to tune and thereby extend the QD ground state to longer wavelengths is expected to provide QD solar cells with an additional infrared contribution to the PC. Moreover, the GaAsSb CL could assist the escape of holes in type-I structures through a two-step mechanism [106], facilitating carrier extraction from the nanostructures. Indeed, the introduction of an additional energy level between the QD ground state and the GaAs barrier would serve as a middle step for holes. This would reduce the hole escape time, exponential-dependent with the barrier energy, significantly increasing the extraction probability. In addition, the use of higher amounts of Sb in the CL should lead to an extended absorption edge, while switching to a type-II band alignment. The use of type-II structures has already been proposed for solar cell applications, in which they are predicted to provide additional benefits [209–212]. Indeed, type-II nanostructures have already been used leading to improved J_{sc} as compared to a reference sample [213,214]. Moreover, recent findings make type-II structures also promising for concentration photovoltaics. Sunlight concentration has been found to suppress the recombination activity in type-II QDs [215], as well as to provide a fast recovery of the V_{oc} in type-II QR solar cells [216], as a consequence of the higher radiative lifetimes. This all motivates the study of the impact of both type-I and type-II QD-CL band alignments on the performance of QD solar cells. To do that, Sb contents within both band-alignment regimes will be used.

6.2. Sample description

A series of three p-i-n junction solar cells (Fig. 6.1) were grown whose active region consists of ten InAs QD layers grown at 450 °C by depositing 2.8 MLs at $\sim 0.04 \text{ ML s}^{-1}$. The QD layers were covered by a 20 ML-thick $\text{GaAs}_{1-x}\text{Sb}_x$ CL grown at 470 °C with nominal Sb contents of 0, 10, and 20% (samples S-0, S-Sb_I, and S-Sb_{II}, respectively). The CLs in S-Sb_{II} were grown at 1 MLs^{-1} , while in S-Sb_I, CLs were grown at 2 MLs^{-1} keeping the Sb_4 flux constant in both samples. As it will be shown in Section 7.3.3.1, the sticking coefficient of Sb for capping rates between 1 and 2 MLs^{-1} is expected to be close to unity and, therefore,

the Sb content in the CLs in S-Sb_I is expected to be half that in the CLs in S-Sb_{II}.¹ A 10 ML-thick LT GaAs layer was grown immediately after the CL at the same temperature, afterwards increasing the substrate temperature to 580 °C for the 35 nm-thick GaAs spacer growth, in order to avoid the formation of extended defects [217,218]. In addition, a control GaAs sample, with no QDs inside, was grown for comparison. Due to the comparative nature of this study, a simple device structure was chosen so no window layer or antireflection coating was used (parameters such as the doping levels or the emitter and intrinsic region thicknesses are not either optimized). The whole active region was sandwiched in the middle of a 400 nm-thick intrinsic GaAs layer, grown on a 500 nm-thick n-GaAs base buffer and ended in a 350/150 nm-thick p-/p⁺-GaAs layer. Mesa-processed solar cell devices with 200 µm diameter were finally fabricated following the procedure described in Section 3.4.

Fig. 6.1: Sketch of the p-i-n solar cells containing ten stacked InAs QD layers capped with a thin GaAsSb CL.

¹ As shown in section 2.5, the addition of 10% Sb to the CL already induces a strong preservation of the QD and, therefore, the effect of the capping rate is not expected, in principle, to significantly affect the final QD size and geometry.

6.3. Results and discussion

6.3.1. Compositional and structural analysis

The Sb content in the CL was first estimated in cross sectional TEM samples by 1 nm probe EDX. The amounts for samples S-Sb_I and S-Sb_{II} were found to be approximately 10 and 24%, respectively, in agreement with the nominal values. Fig. 6.2 (a), (b), and (c) show g002 dark-field X-TEM images taken on the [110] pole axis of representative global views from the ten stacked QD layers in samples S-0, S-Sb_I, and S-Sb_{II}, respectively. Through this chemically sensitive imaging mode, the Sb-containing layers are distinguished by a brighter contrast so that averaged CL thicknesses of approximately 5.5 nm were estimated in both Sb-containing samples. While samples S-0 and S-Sb_I present flat growth fronts all through the stacked layers (Fig. 6.2 (a) and (b)), the growth front in sample S-Sb_{II} progressively bends as the number of stacked layers increases (Fig. 6.2 (c)). In this case, the high Sb content is leading to a highly-strained structure, resulting in the origination of extended defects. This difference can be clearly observed in the bright-field images (Fig. 6.2 (d), (e), and (f)), taken along the 220 g-vector direction. Besides the typical contrast associated to the QDs, the presence of threading dislocations, generated at the bottom layer and crossing upwards through the whole structure, is revealed in S-Sb_{II}. Since the QDs are not strain-coupled, they are not vertically aligned in our structures, so that the effect of Sb on the alignment homogeneity of the QDs suggested elsewhere [207] will not be involved in the device performance in our case. For clarity's sake, a sketch of the expected QD-CL band structure for a single layer in each sample is represented in Fig. 6.2 (g), showing the expected type-I and type-II band alignments in S-Sb_I and S-Sb_{II}, respectively.

Fig. 6.2: g002 dark-field X-TEM images at the [110] pole displaying representative global views of the ten stacked QD layers in samples S-0 (a), S-Sb_I (b) and S-Sb_{II} (c). A brighter contrast differentiates GaAsSb CLs from the darker WL-QD. Bright-field images using the 220-diffraction condition from similar regions in S-0 (d), S-Sb_I (e) and S-Sb_{II} (f), reveal the presence of extended defects in S-Sb_{II}. Scale bar, corresponding to 100 nm, is valid for Figs. (a) to (f). (g) Sketch of the expected band structure in samples S-0, S-Sb_I, and S-Sb_{II}, from left to right.

Fig. 6.3 (a) shows HR-XRD θ -2 θ scans around the (004) reflection for samples S-0, S-Sb_I, and S-Sb_{II}. The shift of the superlattice mean peak (S(0)) to a lower angle with respect to the GaAs substrate Bragg angle in sample S-0 is a fingerprint of compressive strain, which has been induced by the InAs QD insertion into the GaAs matrix. The accumulation of additional compressive strain due to the introduction of Sb-containing CLs is directly reflected by an additional shift of the superlattice mean peak, increasing with the Sb content. The HR-XRD measurements, which average out the information over an extended sample area, allow estimating an average superlattice period, found to be 40 nm in Sb_I, 43 nm in Sb_{II}, and 48 nm in S-0, in a good agreement with values found from local TEM measurements: 40, 44,

and 50 nm, respectively. The significantly longer period for S-0 is a consequence of a deviation from the nominal growth rate (1 ML s^{-1}). X'Pert Epitaxy software was used to make additional estimates for the Sb content in the CLs from the measured XRD spectra. Simulated spectra for S-Sb_I and S-Sb_{II} are depicted in Fig. 6.3 (a) as semitransparent curves. Using a superlattice period thickness of 40 nm (S-Sb_I) and 43 (S-Sb_{II}), as determined by XRD, and the CL thickness of 5.5 nm found by TEM, it is only necessary defining a thickness for the WL in order to determine the Sb content in the CL. Assuming therefore a WL thickness of 0.5 nm [106] leads to Sb content estimates of 10.0% and 19.0% in S-Sb_I and S-Sb_{II}, respectively. The estimation for S-Sb_I (10.0%) is in perfect agreement with the value found by EDX (10%). In the case of S-Sb_{II}, a somewhat lower amount of Sb is drawn from the HR-XRD simulation (19% vs. 24% EDX estimation). Since the GaAsSb CL is not homogeneous, with an accumulation of Sb in the upper interface and a depletion just above the WL, the punctual EDX measurements made just in the Sb-rich region [184] could be the origin of the higher values observed as compared to the HR-XRD results in S-Sb_{II}. The normalized PL spectra from this set of samples is also represented in Fig. 6.3 (b) revealing a direct correlation between the PL FWHM and the increase of accumulated strain with the Sb content. This tendency is not followed in single QD-layer samples, wherein similar amounts of Sb in GaAsSb CLs induce a reduction of the FWHM [108]. This implies that strain becomes the dominant factor affecting the PL linewidth for ten stacked QD layers.

Fig. 6.3: (a) θ -2 θ XRD scans around the (004) Bragg reflection performed on samples S-0, S-Sb_I, and S-Sb_{II}, revealing an increasing accumulation of strain with increasing Sb content. (b) Normalized PL spectra from the set of samples showing an increasing FWHM (indicated along with the normalized PL) with the increase of strain accumulation.

6.3.2. Band structure simulation

In order to model our structures, theoretical simulations have been performed at Instituto de Microelectrónica de Madrid (IMM) by J. M. Llorens. Simulations have been carried out on the electronic structure of two independent systems, which will help us in the development of the forthcoming discussion. The first system comprises a single QD on top of a WL and covered by a GaAsSb CL (QD-CL). The stacking effect is introduced in the calculation by imposing periodic boundary conditions along the growth axis. The second system is a superlattice which contains three layers, namely the WL, the GaAsSb CL and the GaAs spacer (WL-CL). We have proceeded in this way to identify the electronic structure of the WL in the inter-dot region. The direct procedure of extending the simulation region to describe simultaneously the QD and the inter-dot region would have required computational resources far from our current capabilities.

Fig. 6.4: (a) Sketch of the QD-CL geometry considered in the calculation. (b) Energy estimated for the fundamental transition of the QDs for different Sb contents in the CL together with a cross-section in the plane (110) of the hole ground state probability density.

The QD has been theoretically modeled considering the structural data obtained by TEM and HR-XRD. A scheme depicting the most relevant geometrical parameters in our description of the nanostructure is shown in Fig. 6.4 (a). The Nextnano++ package [219] was used to solve the eight multiband Schrödinger equation and determine the electronic structure. All material parameters were extracted from Ref. [220]. Since self-assembled QDs are the result of a lattice strain relaxation process, the effect of this strain is included in our model to obtain a realistic electronic structure description. In addition, the strain also induces the appearance of piezoelectric charges which results in the formation of an electrostatic potential. We have introduced the effect of this potential, by solving the Poisson's equation. The QD-CL electronic structure has been used to verify the expected band alignments in S-Sb_I and S-Sb_{II}. The QD is represented by a hemi-ellipsoid volume using the averaged estimations from TEM of the base radius and height. The actual geometrical values of radius (R_{QD}) and height (h_{QD}) depend on the Sb concentration, being the values of $\{R_{\text{QD}}, h_{\text{QD}}\}$ in nm: $\{8.5, 4.7\}$ for S-0, $\{8.0, 3.8\}$ for S-Sb_I and $\{9.0, 4.6\}$ for S-Sb_{II} [184]. The WL thickness is fixed to 0.5 nm and the CL to 5.5 nm, as observed by TEM. The gallium content in the QD is fixed to $x = 21.5\%$ to get a good agreement between the theoretical and experimental value of the emission energy of the reference sample (without GaAsSb CL). The evolution of the transition energy with the Sb content is shown in Fig. 6.4 (b). We have also included a cross-section of the hole ground state density of probability to show how the increase of Sb in the CL is responsible for a transition from type-I to type-II band alignment. The hole is confined within the QD for zero and 10% Sb content, while for 24% the wave function is expelled out the nanostructure, being localized in the CL [106]. Such a change in the type of band alignment has a great impact on the recombination rate. Indeed, the computed radiative lifetime is 0.50 and 0.52 ns for S-0 and S-Sb_I, respectively, and significantly larger for S-Sb_{II}, 60 ns.

Similarly, the WL-CL band structures have also been simulated using the same thicknesses considered above (0.5 and 5.5 nm, respectively). The evolution of the periodic (WL-CL-GaAs) band structure, with 0%, 10% and 25% Sb contents in the CL, is depicted in Fig. 6.5, where the red and blue continuous curves represent the hole and electron wavefunction, respectively, at the ground states (horizontal lines). As observed, the structure shows a type-II band alignment in both S-Sb_I and S-Sb_{II}, in which the holes are delocalized towards the GaAsSb CL. Fig. 6.6 shows the estimated WL-CL ground state energy and radiative lifetimes as a function of the Sb content. The energy for the InAs WL transition (sample S-0) is estimated to be 1304 meV. The position of the ground state transition corresponds to an energy of 1202 meV in case of S-Sb_I (Sb content of 10%) and ranges between 1069 - 999 meV for S-Sb_{II}, (Sb content of 19-24%, according to HR-XRD and EDX, respectively). Radiative lifetimes were estimated at ~ 1.1 ns for S-Sb_I, and ranging between 2.7 and 4.0 ns for S-Sb_{II}, significantly increasing with respect to that in a simple InAs WL (0.7 ns). Such an increase is a consequence of the transition to a type-II band alignment; its possible impact on solar cell performance is commented hereafter.

Fig. 6.5: Band structure of the WL-CL-GaAs structure for 0, 10, and 25% Sb contents. The red and blue continuous curves represent the hole and electron wavefunction, respectively, at the ground states (horizontal lines).

Fig. 6.6: Dependence of the ground state transition energy and the radiative lifetime in the WL-CL-GaAs structure with the Sb content.

6.3.3. Photocurrent analysis

Representative PC spectra from sample S-0, S-Sb_I, and S-Sb_{II}, are represented in Fig. 6.7 (a), (b), and (c), respectively. Relatively small dispersion was found testing a number of tens of devices within each sample. Normalized EL measurements of the very same devices under different injection current densities are also shown under the PC curves in order to verify the position of the QD ground state transition as well as to confirm the type-II band alignment in S-Sb_{II}, which is verified by the shift of the EL peak to higher energies when increasing injection current [158]. A significant contribution from the QDs to the PC is observed in sample S-0, both from the ground and first excited states. The WL is also providing a strong contribution, whose position matches quite well with the value previously estimated from simulations, which is indicated with a vertical line. On the other hand, the presence of the CL in S-Sb_I extends the absorption edge to longer wavelengths through the tuning of the QD ground state. PC from the ground state shows now an absorption edge broader than in the case of S-0, as expected from the PL FWHM at 15 K. Moreover, the CL itself is also giving rise to a strong contribution to the PC. In fact, a clear shoulder is observed at the wavelength estimated for the WL-CL ground state. Hence, the introduction of the CL makes the QD solar cell work as a hybrid QD-QW solar cell. The higher Sb content in the CL extends even further the photoresponse in S-Sb_{II}. In this case, the EL peak under low injection current densities defines the QD ground state and matches with the absorption edge observed in PC at long wavelengths, so that it can be ascribed to the absorption from the type-II QDs. The QD ground state energy is not properly reproduced by the model in S-Sb_I (further work is needed in this case), but it is accurately predicted in S-Sb_{II}. For higher injection current densities, the ground state shifts to higher energies, owing to the carrier-induced band bending, typical for type-II structures [158]. Moreover, a new emission peak arises at around 1130 nm (1097 meV) at high injection currents. This peak is located close to the ground state transition calculated for the WL-CL according to the average Sb content estimated by HR-XRD (19%) and gives rise to the absorption shoulder observed in PC at the same wavelengths. The PC spectra from all the samples are shown together in Fig. 6.7 (d), along with that of the GaAs reference sample for a clear comparison of the PC evolution with the addition of the QD layers and the increase of the Sb content in the CL. A clear enhancement of the PC in the long wavelength region is observed with the Sb content, being extended beyond 1.5 μm in S-Sb_{II}.

Fig. 6.7: RT PC spectra from S-0 (a), S-Sb_I (b), and S-Sb_{II} (c). Vertical lines point out the calculated position for the WL-CL structure ground state. Normalized EL spectra at 3 (blue), 30 (gray), 150 (dark gray), 300 (black), and 600 (navy) A/cm² are displayed under each PC curve, confirming the position of the QD ground states, as well as that of the WL-CL in S-Sb_{II}. The type-II band alignment in S-Sb_{II} is revealed by the strong shift of the EL peak to higher energies when increasing injection current. (d) PC curves from all the samples together with the GaAs reference sample for a direct comparison.

The introduction of QWs in the host material has been found to affect the transport of carriers drifting through the structure. This has been clearly observed, for instance, in N-containing structures, where the electron trapping is intensified by the strong impact of N in the conduction band [221,222]. Only a slight reduction of the collected carriers photogenerated in GaAs would be sufficient to significantly reduce the overall PC, so that the possible negative impact of the CL might be critical for the final solar cell performance [222]. Indeed, I-V measurements revealed that a complete carrier collection, reflected in a saturation of the photogenerated current [223], is only achieved in all the samples under reverse bias conditions. This can be observed in Fig. 6.8, showing the PC from the GaAs reference sample, S-0, S-Sb_I, and S-Sb_{II} measured at 0 V and -3 V, the latter bias ensuring complete carrier collection in all samples. Biasing had no impact on the GaAs reference sample with no QDs, in

which a complete carrier collection is already achieved under short-circuit conditions (0 V), so that the enhancement observed in the PC of S-0, S-Sb_I, and S-Sb_{II} must be due to other factors affecting carrier collection efficiency, rather than to a possible enlargement of the depletion region or the presence of not negligible parasitic resistances.

Fig. 6.8: RT PC spectra from the GaAs reference sample (a), S-0 (b), S-Sb_I (c), and S-Sb_{II} (d) at 0 V and -3 V bias.

In order to evaluate the impact on carrier transport and the contribution from the nanostructures to the PC, the integrated PC at both 0 V and -3 V has been evaluated. Table 6.1 shows the integrated PC calculated in two distinguished regions. PC_{GaAs} designates the integrated PC between 1.37 and 1.6 eV (775 – 905 nm), roughly corresponding to the GaAs contribution to the PC in the measured range of wavelengths, while PC_{QD-CL} designates the integrated PC for energies below 1.37 eV, quantifying the contribution of the QD-CL structures. For a simpler comparison, both values have been normalized to that of PC_{GaAs} in the GaAs reference sample, the highest measured value under 0 V conditions. The relative increase $\Delta PC = [PC(-3 V) - PC(0 V)] / PC(0 V)$, is also shown in Table 6.1 as a percentage for both ranges of wavelengths.

	PC _{GaAs}			PC _{QD-CL}		
	0 V	-3 V	Δ PC _{GaAs} (%)	0 V	-3 V	Δ PC _{QD-CL} (%)
GaAs	1	1	0	-	-	-
S-0	0.94	1.14	21	0.13	0.21	62
S-Sb _I	1	1.13	13	0.31	0.38	23
S-Sb _{II}	0.84	1.10	31	0.47	0.62	32

Table 6.1: Estimation of the integrated PC between 1.37 and 1.6 eV (PC_{GaAs}), related to the GaAs absorption, and for energies under 1.37 eV (PC_{QD-CL}), corresponding to the contribution from the nanostructures (QD-CL). The estimations under 0 and -3 V are shown, roughly corresponding to electric fields in the intrinsic region of 17.5 kV/cm and 55 kV/cm, respectively. For a simpler comparison, all the values have been normalized to that of PC_{GaAs} in the GaAs reference sample, the highest measured value under 0 V conditions. Δ PC represents the relative increase for both ranges of wavelengths, which is defined as Δ PC=100 • [PC(-3 V)-PC(0 V)]/PC(0 V).

The main conclusions drawn from the values in Table 6.1 are the following:

- The comparison at 0 V reveals that the presence of InAs QDs is hindering the collection of carriers photogenerated at GaAs. Nevertheless, this effect is partially inhibited by the introduction of the GaAsSb CL. This is evidenced by the improved PC_{GaAs} in S-Sb_I as compared to S-0 under short-circuit conditions and by the smaller Δ PC_{GaAs}. This suggests that the sole presence of a thin WL might be affecting the transport of carriers through the structure, as it has already been proposed in other devices [187], and that the type-II band alignment exhibited by the WL-CL structure leads to a more efficient carrier collection at 0 V. Indeed, since the relative section occupied by the QDs is only a fraction around 10% of the overall device section, estimated from AFM measurements, the trapping of carriers drifting through the structure must occur most likely at the WL. As shown in Section 6.3.2, the type-II band alignment increases carrier radiative lifetime in the WL as compared to the reference sample S-0, which would reduce radiative recombination of trapped carriers and facilitate thermal carrier escape and electric field-assisted collection. Since carriers photogenerated at GaAs have the highest relative weight in the overall PC, avoiding losses of carriers trapped at the WL has a significant impact on the device performance.
- The analysis at reverse bias shows a much smaller relative increase of PC_{QD-CL} from 0 V to -3 V in both S-Sb_I and S-Sb_{II} than that in S-0 (23 and 32% vs. 62%, respectively). This indicates an improved carrier extraction from the nanostructures with the addition of the GaAsSb CL. This could be likely related to a two-step hole escape

mechanism in the type-I structure (from the QD to the GaAsSb CL and from the CL to the GaAs barrier) and to the longer hole lifetimes in the type-II sample.

- The use of a high Sb content induces a lower PC_{GaAs} in S-Sb_{II} at 0 V as compared to the other samples. This is expected both from the presence of extended defects and the introduction of deep hole levels in the structure. Remarkably, the relative increases in PC_{QD-CL} and PC_{GaAs} in S-Sb_{II} are approximately the same (32% vs. 31%, respectively). This suggests that, in this sample, a mechanism other than carrier trapping or a hindered extraction from the nanostructures is involved in the incomplete carrier collection under short-circuit conditions, affecting in a similar extent carriers photogenerated in any region of the device. It is known that, in the presence of defects, the collection efficiency strongly depends on the thickness of the intrinsic region and the drift lengths of carriers which, in turn, directly depend on the carrier lifetime and the built-in field [224]. In the case of S-Sb_{II} it can be assumed that defect-induced SRH non-radiative recombination is reduced by stronger built-in fields, increasing drift lengths and allowing a more efficient carrier collection by the application of reverse bias [225].
- Despite the presence of extended defects, S-Sb_{II} shows the highest contribution from the nanostructures. Indeed, PC_{QD-CL} at 0 V increases with the Sb content. This enhancement is due to the extension of the absorption edge to longer wavelengths, the strong contribution of the CL, and the type-II WL-CL structure. In addition, despite the lower PC_{GaAs} due to the presence of defects, the overall integrated PC under short-circuit conditions in S-Sb_{II}, i.e., the addition of PC_{GaAs} and PC_{QD-CL} , is as high as that in S-Sb_I, strongly exceeding it at -3 V. Hence further benefits are expected from such structures if the creation of dislocations is inhibited, what would allow improved carrier collection efficiencies for higher Sb contents, providing a higher J_{sc} . This is feasible, for instance, through strain-balancing techniques, such as the use of N- or P-containing strain-compensating spacer layers [124,226–228].

6.3.4. Solar cell performance

Fig. 6.9 shows the J-V characteristics under AM1.5D illumination of samples S-0, S-Sb_I, and S-Sb_{II} together with that of the GaAs reference sample. The reference sample shows a low J_{sc} and V_{oc} as compared to common values for GaAs solar cells due to the unoptimized structure of the devices designed for the comparative study on the impact of the CLs. Indeed, the efficiency of the reference sample is 3.94%, quite low as compared to typical values in cells with an optimized design. The introduction of InAs QDs in S-0 leads to an expected reduction of the V_{oc} of 0.145 V. However, also a drop is observed as to its J_{sc} resulting in a conversion efficiency of 2.16%. In particular, the drop observed in J_{sc} is expected from the previously discussed incomplete carrier collection under short-circuit conditions induced by

the introduction of QDs. The use of the GaAsSb CL in sample S-Sb_I induces an additional small reduction of 0.033 V in V_{oc} with respect to S-0 ($V_{oc} = 0.585$ V). Nevertheless, J_{sc} is increased by almost 15%, slightly exceeding that of the GaAs reference sample. In S-Sb_{II}, V_{oc} is further decreased in 0.059 V, while J_{sc} remains virtually unaltered, as compared to S-Sb_I. Hence, although S-Sb_I and S-Sb_{II} show a lower conversion efficiency as compared to the GaAs reference solar cell, they exceed that of S-0 by 20% and 10%, respectively. This occurs despite the significant introduction of additional accumulated strain and, in case of S-Sb_{II}, extended defects [229]. The extended PC, the contribution from the CL and the improved carrier collection discussed previously are likely behind the conversion efficiency enhancement.

Fig. 6.9: J-V characteristics of samples S-0, S-Sb_I, and S-Sb_{II}, together with that of the control sample, under 900 W/m² AM1.5D conditions.

Finally, the impact of light concentration on V_{oc} has been analyzed, as described in section 3.5.5.2, in the QD samples. Fig. 6.10 (a) shows dark I-V curves from S-0, S-Sb_I, and S-Sb_{II}. Ideality factors of 1.40 (S-0), 1.36 (S-Sb_I), and 1.36 (S-Sb_{II}) were drawn by fitting the exponential regime of the curves to the diode equation (Eq. 3.9). The expected V_{oc} according to these ideality factors are represented by dashed lines in Fig. 6.10 (b), along with the measured monochromatic V_{oc} as a function of the light power. The V_{oc} of S-0 follows the expected evolution, consistently with the diode equation. Remarkably, V_{oc} in S-Sb_{II} follows an increasing tendency with light power faster than expected from the dark I-V curve. Indeed, the V_{oc} of S-Sb_{II} exceeds that of S-0 under high light power (0.94 vs. 0.92 V). This fact means that light concentration is balancing the impact of introducing a lower effective band gap within the host material in these structures: the V_{oc} is not limited by the low band gap of the CLs, contrary to what happens in the case of using thicker GaAsN barriers [230]. Although

the faster V_{oc} increase in this sample could be partially due to the presence of defect-related non-radiative recombination, other effects must be present or otherwise the V_{oc} could never be larger than that of the reference sample. A faster V_{oc} increase could also be expected in S-Sb_{II} at low concentrations due to the Stark effect, but this would never lead to an V_{oc} higher than that in a type-I structure. Indeed, the current generated using the highest light power is close below 30 A/cm^2 , which was used for one of the EL measurements (gray curve in Fig. 6.7 (c)). As can be observed in Fig. 6.7 (c), the EL peak at such injection currents is clearly located below the energy corresponding to the V_{oc} (0.90 eV and 0.94 V, respectively). This means that in S-Sb_{II} high light concentrations lead to an V_{oc} higher than the effective band gap (defined by the QD ground state). This must be induced by a faster quasi-Fermi-level splitting with injection current following the faster population of the QD electronic states with light power because of the much longer radiative lifetimes in the type-II QD-CL structures. Indeed, EL emission from QD excited states and even from the WL-CL is observed in this sample at injection current levels for which emission in S-0 and S-Sb_I only occurs at the QD ground state (Fig. 6.7).

Regarding S-Sb_I, the V_{oc} follows the tendency expected from the dark I-V curve for low light power densities, switching to a faster increasing tendency under higher light concentrations and also leading to an V_{oc} slightly higher than in S-0. A high light power regime is also observed in S-Sb_{II}, starting from some lower light concentration. Although further research is necessary for a good understanding, this behavior is likely related to the type-II WL-CL band structure in both S-Sb_I and S-Sb_{II}.

Fig. 6.10: (a) Dark I-V curves at RT from samples S-0, S-Sb_I, and S-Sb_{II}. (b) V_{oc} under 781 nm laser illumination as a function of the light power density. Dashed lines represent the expected V_{oc} according to the ideality factors drawn from the dark I-V curves.

6.4. Conclusions

In conclusion, we have presented a study on the effect of using thin GaAsSb CLs for InAs QD solar cells with two different Sb contents providing QD-CL structures with type-I and type-II band alignments. The QD absorption can be extended by increasing the Sb content in the CL, achieving photoresponse up to beyond 1.5 μm in the type-II structure. The CL provides a strong additional contribution to the PC, and is found to improve the carrier collection efficiency of a reference QD solar cell, likely due to the type-II WL-CL band alignment. Indeed, the WL-CL band alignment seems to have a stronger impact on the overall solar cell performance than the QD-CL band alignment under 1 sun illumination. An efficiency improvement of up to 20% as compared to the reference QD solar cell has been obtained when using a moderate Sb content. For high Sb contents, despite the larger contribution from the nanostructures to the PC, the efficiency improvement is reduced to 10%. The presence of dislocations due to excessive accumulated strain is probably the main reason behind this effect. Nevertheless, an especially faster V_{oc} increase is found under light concentration in this case, slightly exceeding that of the reference QD solar cell in both Sb-containing devices. Remarkably, a V_{oc} higher than the effective band gap is achieved in the sample with a type-II QD-CL band structure under high light concentration. The type-II band alignment in both the QD-CL and the WL-CL structures appears as a competing factor, allowing an enhanced improvement of the V_{oc} under light concentration.

Part III: GaAsSbN/InAs/GaAs quantum dots

The strain-compensating effect of GaAsN CLs used on InAs/GaAs QDs [124] suggests the addition of N in GaAsSb CL as a straightforward solution for the origination of extended defects in stacked GaAsSb/InAs/GaAs QDs or as a means to allow for a higher number of such QD stacks. Moreover, the addition of N to GaAsSb CLs has very recently been demonstrated to enable an independent tuning of the electron and hole confinement inside the QD [128]. This is possible due to the independent effect of N over the conduction band, according to the BAC model [122], being complementary to the effect of Sb on the valence band. Thus, this represents a very versatile system, in which a type-II band alignment can be achieved by modifying either the valence or conduction band. This allows an accurate control of the QD electronic structure, imposing the possible requirements of different optoelectronic applications. In addition, such an approach could be an alternative for the long-wavelength telecommunication window, as well as for QD solar cell applications. The chapters in Part III deal with a growth optimization procedure of InAs QDs capped with GaAsSbN CL and their application to solar cell devices. Chapter 7 is devoted to the improvement of the luminescence properties through different CL growth approaches and Chapter 8 addresses the impact of different GaAs(Sb)(N) CLs on the performance of InAs QD solar cells.

7.1. Introduction

Despite the promising expectations, the growth of the quaternary GaAsSbN faces important epitaxial growth problems due to the simultaneous presence of Sb and N, such as alloy disorder, phase separation (because of its large miscibility gap), clustering, difficult composition control (3 group-V elements competing for the same lattice position), or N-related point defects and localized electronic states (as in any other dilute nitride alloy)[231–233]. Therefore, the growth window of GaAsSbN layers on GaAs is already quite narrow. In our case, the situation is even more complex, since the quaternary will grow on top of an uneven InAs surface and experience an inhomogeneous strain field. Indeed, significant structural changes have been found even in thin (5 nm thick-) CLs [234]. Despite the huge reduction of the strain fields with the incorporation of N to GaAsSb CLs, strain and compositional inhomogeneities are generated during the CL growth yielding the presence of Sb-rich and Sb-poor regions in the range of a few nanometers with a preferential deposition of Sb on top of InAs QDs. This leads to such a degradation of the luminescence that no RT emission is achieved from GaAsSbN/GaAs/InAs QDs [128]. Hence, the growth process must be investigated and optimized before these structures can be applied to any optoelectronic device.

Efforts will initially focus on an attempt to achieve RT PL from this system and extend the emission wavelength towards the IR. First, the different CL growth parameters, such as the CL thickness, growth temperature and growth rate, will be optimized. Such parameters are expected to significantly influence the mass transport phenomena and therefore the composition modulation in the CL. Finally, the growth of the CL in a short-period superlattice-like manner will also be analyzed.

7.2. Sample description

The QD layers in the analyzed samples were always grown under the same conditions by depositing 2.8 MLs of InAs at 450°C and 0.04 MLs⁻¹ on an intrinsic 500 nm-thick GaAs buffer layer. The GaAsSbN CL was grown modifying only one of the growth parameters for each series of samples immediately followed by a 10 ML-thick LT GaAs layer to avoid Sb/N desorption. A 250 nm-thick GaAs layer was then grown at 580 °C, finally depositing on top a layer of uncapped QDs under the same conditions as the buried QD layers for AFM analysis (Fig. 7.1).

Fig. 7.1: Sketch of the samples containing an InAs QD layer capped with a thin GaAsSbN CL.

7.3. Results and discussion

First it is necessary to establish the reference growth conditions for the GaAsSbN CL as a starting point from which one of the parameters will be modified in each series of samples. Thus, as reference conditions for the CL growth, those used in the previous studies for GaAsSb are considered, i.e., a 470 °C growth temperature, a thickness of 5 nm and a growth rate of 1 MLs⁻¹. Regarding the N and Sb contents, a power of 140 W for the RF plasma source and a temperature of 335 °C for the Sb effusion cell were chosen as reference source conditions. These conditions correspond in our system to nominal contents of 2.5% of N and 15% of Sb. In order to support the accuracy of these values, three samples consisting of single GaAsSb, GaAsN and GaAsSbN QWs were also grown under the same reference conditions, whose normalized 15 K PL is shown in Fig. 7.2. The band gap determined by the PL peak position of the GaAsSb and GaAsN QWs corresponds to Sb and N contents of ~15% and ~2.3%, according to experimental results for such GaAsSb and GaAsN QW thickness [235,236]. The 15 K PL from the quaternary QW sample shifted from the GaAs gap energy a higher value (527 meV) than the addition of the shifts in the GaAsSb (216 meV) and GaAsN (255 meV) QW samples. This is in agreement with studies reporting a facilitated incorporation of N by the presence of Sb [237,238]. Indeed, the difference of 56 meV points to a higher N content corresponding to ~2.8%. The estimated Sb and N contents in the ternary and quaternary CLs are summarized in table 7.1. For these N and Sb contents the QD-CL system will still be in the type-I band alignment region [128]. Furthermore, since the Sb/N ratio (15/2.8) is larger than ~2.8, the condition for lattice-matching to GaAs [239], it can be assumed that the GaAsSbN layer grows under compressive strain on GaAs and will act as a strain-reducing CL.

Fig. 7.2: PL spectra at 15 K for GaAsSb, GaAsN, and GaAsSbN QWs grown under the reference conditions for the CL and using the reference Sb and N source conditions.

CL	Sb (%)	N (%)
GaAsSb	15	---
GaAsN	---	2.3
GaAsSbN	15	2.8

Table 7.1: Estimation of the Sb and N contents in ternary and quaternary CLs grown under reference conditions.

7.3.1. Capping layer growth temperature

First, the study focuses on finding the optimal growth temperature for the GaAsSbN CL. The incorporation of N in GaAs has been found to be temperature-independent in a wide range of temperatures from 400 °C to ~ 480 °C [240] or even higher temperatures [241,242]. However, for temperatures higher than that, N incorporation is strongly reduced. This is probably induced by the temperature-enhanced desorption of N from the growth surface, as it has been theoretically predicted [243]. On the other hand, as expected from the fact that Sb has a higher sublimation energy than As [244], increasing the temperature affects substantially the incorporation of Sb [245,246]. Thus, Sb desorption has been found to increase with temperature, becoming substantial above 490 °C [245]. Hence, in order to avoid a significant desorption of both Sb and N, as well as a substantial modification of the InAs QDs, we studied the effect of the CL growth temperature in a range between 450 and 480 °C. A series of four samples was grown with CL growth temperatures set to 450, 460, 470 and 480

°C (labeled as A1, A2, A3 and A4, respectively). Fig. 7.3 shows the PL spectra of the four samples, while the FWHM and integrated intensity are represented in the inset. The small peak wavelength shifts observed do not follow any tendency with the growth temperature, and are likely within the reproducibility error bar. Nevertheless, an improvement of the luminescence properties can be observed with increasing the growth temperature from 450 up to 470 °C, being more remarkable for the last temperature case. The FWHM is slightly reduced and the integrated intensity is approximately doubled when raising the temperature within this range. However, above 470 °C the integrated PL intensity is reduced by ~65% and the FWHM is slightly increased. Hence, the reference CL growth temperature, 470 °C, provides the best PL properties in GaAsSbN/InAs/GaAs QDs.

Fig. 7.3: PL spectra at 15 K from samples with the CL grown at different temperature. The inset shows the integrated intensity and the FWHM of the PL spectra as a function of the CL growth temperature. Lines are guides to the eye.

7.3.2. Capping layer thickness

In order to analyze the impact of the CL thickness on the PL properties, a series of samples with a 2.5, 5.0 and 7.5 nm-thick GaAsSbN CL was grown (samples B1, B2 and B3, respectively). Fig. 7.4 shows the 15 K PL spectra of the three samples, while the FWHM and integrated intensity are represented in the inset. Reducing the CL thickness from 7.5 to 2.5 nm induces a considerable blue-shift, leading also to a decrease of ~20 meV in the FWHM and to a significant enhancement in the integrated intensity by a factor of ~15. Thus, a clear tendency of the PL properties with the CL thickness can be observed, whereby the peak wavelength is red-shifted as the CL thickness increases, accompanied by a significant degradation of the radiative efficiency. This red-shift could arise from several mechanisms.

First, a thicker strain-reducing CL should induce a reduction of the compressive strain inside the QD. Second, and as it happens in GaAsSb-capped QDs [247], the QD size may be larger for thicker GaAsSbN CLs. The degradation of the radiative efficiency is likely originated by a higher composition modulation in the CL. Indeed, a higher composition modulation is expected for thicker CLs, since they accumulate a larger amount of strain, yielding a more pronounced interface roughness. This clustering and roughness would directly act trapping carriers, affecting the carrier injection efficiency into the InAs QDs and decreasing the radiative efficiency of the PL.

Fig. 7.4: PL spectra at 15 K from samples with different CL thicknesses. The inset shows the integrated intensity and the FWHM of the PL spectra as a function of the CL thickness. Lines are guides to the eye.

7.3.3. Capping layer growth rate

A series of samples was grown wherein the only modified parameter was the growth rate of the quaternary GaAsSbN CL, while the rest of the growth parameters were kept at their reference values. Five samples with CL growth rates of 0.5, 1.0, 1.2, 1.5 and 2.0 MLs⁻¹ were grown (samples C1, C2, C3, C4 and C5, respectively). Fig. 7.5 shows the PL spectra from this series of samples with their integrated intensity and FWHM evolution depicted in the inset. A significant enhancement of the PL properties with the growth rate is observed. The integrated intensity is improved up to 40 times when going from 0.5 to 2.0 MLs⁻¹, and the FWHM is reduced to ~38 meV for rates above 1.2 MLs⁻¹. Moreover, samples with the CL grown at and above 1.2 MLs⁻¹ showed RT luminescence (the RT PL results will be discussed below). However, the emission is significantly blue-shifted when increasing the CL growth

rate, which suggests a reduced N and/or Sb incorporation in the CL besides a possible impact on the QD size.

Fig. 7.5: PL spectra at 15 K from samples grown with different CL growth rates. The inset shows the integrated intensity and the FWHM of the PL spectra as a function of the CL growth rate. Lines are guides to the eye.

In order to analyze the impact of the growth rate on N- and Sb-containing structures individually, samples either with a GaAsN (samples N1 and N2) or a GaAsSb (samples Sb1 and Sb2) CL were also studied. The CL growth rates were 1 and 2 MLs^{-1} for N1/Sb1 and N2/Sb2, respectively. All these samples were grown under the same conditions as the quaternary counterpart. Fig. 7.6 (a) shows the PL spectra for the GaAsN CL grown at 1 and 2 MLs^{-1} . A blue-shift together with a strong PL improvement can be also here observed when increasing the growth rate of the CL, as it happens for the case of the quaternary. Since the N incorporation was found to be inversely proportional to the growth rate [240,242], the blue-shift can be mainly attributed to a reduced N content. Thus, the sample with the CL grown at 2 MLs^{-1} has a lower N concentration than the 1 MLs^{-1} CL sample.

In order to decouple the effect of the N concentration on the PL properties from that of the growth rate, a third sample was grown at 1 MLs^{-1} (N3). The N RF plasma source power was decreased until the PL peak energy matched that of N2 ($P=100$ W), i.e., until the N concentration was the same. A comparison of the PL from samples N2 and N3 (equal N concentration and 2/1 MLs^{-1} growth rates, respectively) now clearly shows that the PL improvement at higher growth rates is not only due to a reduced N incorporation, but also to an improved structural quality of the CL.

In the case of the GaAsSb CL, a blue-shift and a moderate PL enhancement is observed with increasing growth rate (Fig. 7.6 (b)), also indicative of a lower Sb incorporation. Like

in the case of the GaAsN CL, a third sample was grown to decouple the effect of the growth rate and the Sb concentration. This sample (Sb3) had a lower Sb content to match that of Sb2 (similar PL peak energy), and a 1 MLs^{-1} CL growth rate. Contrary to the case of GaAsN, increasing the growth rate while maintaining the Sb content constant seems to produce a minimum improvement of the PL (see the PLs from Sb2 and Sb3 in Fig. 7.6 (b)). Thus, we can conclude that the sole increase of the growth rate (samples Sb1 and Sb2) leads to a decreased Sb content that is entirely responsible for the improved PL. Indeed, it has been shown that the PL of GaAsSb-capped InAs QDs is degraded for Sb contents above $\sim 12\%$ [108], so a small reduction of the initial content ($\sim 15\%$) should result in an improved PL.

Fig. 7.6: (a) PL spectra at 15 K from InAs QDs capped with GaAsN CL grown at 1 and 2 ML s^{-1} (N1 and N2, respectively), along with that of a sample with the GaAsN CL grown at 1 ML s^{-1} using a lower RF plasma source power (N3), to match the wavelength of N2. (b) PL spectra at 15 K from InAs QDs capped with a GaAsSb CL grown at 1 and 2 ML s^{-1} (Sb1 and Sb2, respectively), along with that of a sample with the GaAsSb CL grown at 1 MLs^{-1} using a lower Sb flux (Sb3) to match the wavelength of Sb2.

7.3.3.1. Quantification of the Sb/N content reduction

In order to determine the reduction of the Sb and N contents when growing the CL at the highest rate, samples consisting of single GaAsSb, GaAsN and GaAsSbN QWs were grown at 1 and 2 MLs^{-1} by using the reference source conditions. Fig. 7.7 shows the PL spectra from these samples, where PL from samples grown at 1 MLs^{-1} appears as dashed lines while that from samples grown at 2 MLs^{-1} is represented by continuous lines. Regarding the GaAsSb QWs (red lines), the increase in the growth rate induces a blue-shift of 101 meV, from which a significant reduction of the Sb content of $\sim 8\%$ can be deduced [235]. Likewise, the emission from GaAsN QW (blue lines) is also strongly blue-shifted as a consequence of the reduced N incorporation. From the blue-shift of 137 meV found for this case, a reduction

of N content of $\sim 1.2\%$ is estimated [236]. The N content is therefore reduced to about half when doubling the growth rate, in good agreement with what is expected from the inverse linear N incorporation dependence on the growth rate [240,242]. In the case of the GaAsSbN QW (black lines), the observed shift is 240 meV, which corresponds very well to the addition of the shift values for the two ternaries, indicating a similar decrease of Sb and N of 8 and 1.2%, respectively. Therefore, Sb and N contents of 7 and 1.6% are expected for the GaAsSbN CL grown at 2 MLs^{-1} so that both elements roughly incorporate proportionally to the inverse of the growth rate and their sticking coefficient can be assumed to be close to unity.

Fig. 7.7: PL spectra at 15 K for GaAsSb, GaAsN, and GaAsSbN QWs grown at 1 and 2 MLs^{-1} . The spectra corresponding to different materials are shifted in the vertical axis for the sake of clarity. Arrows indicate the respective blue-shifts induced by the increased growth rate.

7.3.3.2. Comparison among the three capping layer materials

Fig. 7.8, shows PL FWHM and integrated intensity ratio between the QD samples grown at 2 and 1 MLs⁻¹ for the three cases: the ternaries GaAsSb and GaAsN and the quaternary CL samples. A reduction of the FWHM of ~65% is found for the GaAsN CL sample, stronger than the 25-30% observed for the GaAsSb and GaAsSbN CL samples. On the other hand, the integrated intensity significantly increases for the GaAsN and the GaAsSbN CL samples by a factor of 6.2 and 9.6, respectively. These results show that increasing the growth rate has a particularly strong positive impact in N-containing structures. This could be related to a reduced composition modulation resulting from a lower diffusion of N and Sb atoms on the growth surface. In particular, the reduced FWHM of the PL seems to indicate a homogenization of the CL composition on top of the QDs, where a strong Sb accumulation induced by the presence of N was reported when growing at 1 MLs⁻¹ [234]. Moreover, the shorter time of exposure to the plasma could be attenuating the damage induced by the excited N species, mainly N ions, coming from the plasma source [248]. This would result in a reduced defect density.

Fig. 7.8: Growth rate-induced improvements in the PL spectra for the three CL materials: FWHM and the integrated intensity ratios between 2- and 1-MLs⁻¹ grown CL samples for GaAsSb, GaAsN, and GaAsSbN CLs.

7.3.3.3. Extending the emission wavelength

Our goal is to extend the emission wavelength through the best growth conditions found from the different approaches analyzed above. Since the most significant improvement was found when increasing the growth rate of the CL, the efforts will first focus on trying to extend the emission by adding higher amounts of Sb and N in the CL grown at 2MLs⁻¹. The

reference values will be used for the other parameters. Three samples with the CL layer grown at 2 MLs^{-1} were studied: the first one with the reference parameters for N and Sb sources (sample F1); the second one by raising the Sb effusion cell temperature to 345°C (sample F2); and the last one by increasing both the Sb cell temperature to 345°C and the RF plasma source power to 210 W (sample F3). The PL spectra from this series of samples are shown in Fig. 7.9 (a). It can be observed that increasing the Sb content in the CL leads to a red-shifted emission peak with a simultaneously weakened luminescence. However, it was apparently impossible to incorporate a higher N content at this growth rate, finding a similar spectrum for sample F3 as that of sample F2, with no significant peak shift. This means that the additional active N provided is not being incorporated substitutionally into the lattice.

A similar study was carried out also for a lower growth rate of 1.5 MLs^{-1} . The three samples described in the previous paragraph, with the same parameters for the Sb and N sources, were reproduced with a CL growth rate of 1.5 MLs^{-1} (G1, G2 and G3, respectively). The PL spectra are shown in Fig. 7.9 (b). The PL peak red-shift in sample G2 is now 97 meV , compared to 40 meV at 2 MLs^{-1} . This means that a higher amount of Sb is now incorporated for the same Sb flux than at 2 MLs^{-1} . Moreover, adding higher N contents is still possible at this lower growth rate, resulting in a long wavelength peak close to $1.4 \mu\text{m}$ at 15 K (sample G3).

Fig. 7.9: PL spectra at 15 K when increasing the flux of Sb or Sb and N during the growth of the CL at 2.0 MLs^{-1} (a) and 1.5 MLs^{-1} (b).

This result shows a possible limitation related to N incorporation in the GaAsSbN CL at high growth rates. Indeed, according to the PL peak position and lineshape of F2 and F3 and only under the assumption that the same Sb is incorporated in both samples, N contents

above $\sim 1.6\%$ cannot apparently be incorporated into the lattice when growing the CL at 2 MLs^{-1} . The application of such a high Sb_4 flux and the fast growth rate may prevent active N atoms from finding a favorable anion lattice position, dramatically reducing N sticking coefficient. However, a reduction of the expected contents of both Sb and N, both competing for the same lattice positions, cannot be ruled out.

7.3.3.4. Impact of the capping growth rate on the structural properties

In order to find out the impact of the GaAsSbN CL growth rate on the structural properties of the QDs, the samples with the CL grown at 0.5 (C1), 1.0 (C2), and 1.5 MLs^{-1} (C4) were analyzed by TEM and AFM. The heights of the QDs were measured using the g002 dark-field TEM imaging mode, in which the edges of the QDs are well defined. The QD height distribution measured in the three samples are plotted in a box chart in Fig. 7.10 (a), together with the corresponding histograms. In addition, the height distribution of uncapped surface QDs measured by AFM in sample C2 is represented for comparison (the differences in the surface QDs among the three samples are negligible). g200 dark-field X-TEM images of representative QDs in each sample are also shown in Fig. 7.10 (b), together with an AFM picture of surface QDs. As can be inferred, the growth rate of the alloyed CL has a strong influence on the QD size and shape distribution, with the average QD height decreasing significantly for lower growth rates. The average height is $5.7 \pm 0.8 \text{ nm}$ in C4, QDs capped at 1.5 MLs^{-1} , the QDs showing a pyramidal shape and preserving quite well the original QD height distribution of uncapped QDs (only the very small QDs in the lower tail of the AFM height distribution are eliminated during the capping process). When the growth rate is decreased to 1.0 MLs^{-1} (sample C2), the average QD height decreases to $4.8 \pm 0.7 \text{ nm}$, but the height distribution shows now the presence of two height modes. Indeed, the resulting distribution does not satisfy the Shapiro-Wilk test of normality at the 0.05 level of significance. The height distribution fits to two well defined normal populations with respective heights of $4.2 \pm 0.4 \text{ nm}$ and $5.3 \pm 1.2 \text{ nm}$. Capping with GaAsSbN at 1.0 MLs^{-1} is therefore transforming the original QD distribution into a bimodal one, likely as a result of the inhomogeneous covering of the QDs during the simultaneous deposition of N and Sb [234]. Larger QDs are more favorable sites for Sb accumulation, which may be the reason for a more pronounced inhibition of the QD decomposition [108], giving rise to a preservation of the large QD height population. In contrast, smaller QDs would suffer stronger intermixing, giving rise to the lower-height population. Moreover, the tallest QDs preserve the pyramidal shape observed at higher growth rates, while the QDs of the lower-height population are lens-shaped or truncated pyramids (Fig. 7.10 (b)). Finally, the average QD height is reduced to $4.5 \pm 0.5 \text{ nm}$ when capping at 0.5 MLs^{-1} (sample C1), the QD population fitting again to a single normal distribution. The pyramidal QDs and the large-height part of the original distribution have completely disappeared in this case, all of the QDs showing a lens shape. There is, therefore, a size and shape transition from taller pyramids at high CL growth rates to flatter lens-shaped QDs at low growth rates. Intermediate growth rates around 1 MLs^{-1} seem to be

a transition region between the high and low growth rate populations in which both coexist giving rise to the observed bimodal distribution. As it can be observed, the height distribution becomes narrower for lower growth rates, which have caused smaller QD heights. This means that the QD dissolution process during capping contribute to level the QD heights, resulting in a less dispersed distribution. Both the reduced QD height and size dispersion at lower capping rates were also found for GaAs-capped InAs QDs in Chapter 4. Hence, a similar kinetic mechanism seems to govern the final QD shape, size and distribution in both GaAs- and GaAsSbN-capped InAs QDs.

Fig. 7.10: (a) QD height distributions measured by TEM for samples grown at 0.5 (C1), 1.0 (C2), and 1.5 MLs⁻¹ (C4) plotted in a box chart, together with the corresponding histograms. The box is defined by the 25th and 75th percentiles, where the horizontal line and the solid square in the center of the box are the median and the mean of each population, respectively. The lines extending vertically from the boxes (whiskers) are determined by the 5th and 95th percentiles. (b) g002 dark-field X-TEM images of representative QDs in all the samples, together with an AFM picture of the uncapped QDs.

7.3.4. Room-temperature photoluminescence from different GaAsSbN-capped quantum dots

Fig. 7.11 shows the RT PL spectra from all the samples analyzed in this chapter emitting near 1.3 μm . As it can be observed, RT emission was obtained through different approaches. When using a 2.5-thick GaAsSbN CL (sample B1), RT emission at 1250 nm was obtained. On the other hand, as the low-temperature results suggested, a more intense RT emission can be achieved when increasing the growth rate of the CL. Sample C5 (2MLs^{-1}) emits at 1270 nm with improved luminescence properties, showing an integrated intensity more than twice as large as that of the sample B1, together with a PL linewidth of only 39 meV, virtually the same as at 15 K. Longer wavelengths were achieved from samples with the CL grown at 1.5 (C4) and 1.2 MLs^{-1} (C3), emitting at 1307 and 1329 nm, respectively, but with a more deteriorated luminescence as the growth rate is reduced. By adding a higher Sb content to the CL grown at 2MLs^{-1} , it is also possible to reach peak wavelengths somewhat beyond 1.3 μm . Indeed, sample F2 emits at 1308 nm, showing a significantly more intense luminescence than samples C3 and C4 with a narrower FWHM, which was hardly widened when increasing the temperature from 15 K up to RT. This points again to the benefits provided by the highest growth rate, which allows achieving long emission wavelengths with improved luminescence properties. The obtained results represent a first step towards using GaAsSbN CLs in RT device applications.

Fig. 7.11: RT PL spectra for samples emitting around 1.3 μm .

7.3.5. GaAsSb/GaAsN short-period superlattice capping layer

An intentional separation of the quaternary CL in separated ternary phases could also, in some extent, suppress problems related to the simultaneous presence of Sb and N. This is feasible by the alternate deposition of both ternaries (GaAsSb and GaAsN) in a short-period superlattice-like manner, which would preserve at the same time the electronic versatility of GaAsSbN in the QD-CL structure. Following these considerations, a new series of three samples was grown under the same reference conditions for the CL and the Sb and N sources as described in Section 7.3, using different CLs: a CL containing short-period superlattice consisting of 5 periods of GaAsSb(2ML)/GaAsN(2ML) grown without any interruption between GaAsSb and GaAsN layers deposition (sample SL); a 20 ML-thick quaternary GaAsSbN CL (sample GaAsSbN); and a 20 ML-thick GaAs CL (sample GaAs) as a reference sample. Fig. 7.12 (a) shows the PL spectra at 15 K from the three samples. As expected, the use of the quaternary GaAsSbN CL extends significantly the emission wavelength of InAs QDs but with a strong degradation of the PL. The deposition of the CL as a sequence of both ternaries in sample SL led to a smaller red-shift. This is expected from the lower overall Sb and N content, which should be approximately half than that in sample GaAsSbN. Nevertheless, a significant PL improvement is observed when applying such a CL, both compared to sample GaAsSbN and, remarkably, to sample GaAs. Indeed, the FWHM was reduced from 53 meV in the reference S-GaAs sample to 30 meV, and the integrated intensity increased by a factor of ~ 4 . Moreover, the sample with the standard GaAsSbN CL does not show RT PL, while sample SL shows a strongly improved RT luminescence with respect to the reference (inset in Fig. 7.12 (a)). Noteworthy is the fact that inverting the deposition sequence, i.e., employing a 5 periods-GaAsN(2ML)/GaAsSb(2ML) CL, does not yield significant differences in PL characteristics, revealing that the obtained improvements are not related to the first deposited material, but to the overall SL structure.

According to these results, longer wavelengths at RT could be obtained by adding higher amounts of Sb and/or N to the short-period superlattice. Thus, two new samples were grown: SL2 with nominal Sb and N contents of 25% and 2.5% N, respectively; and SL3 with nominal Sb and N contents as high as 32% and 5%, respectively. The RT PL from these two samples is shown in Fig. 7.12 (b) together with that of sample SL. Sample SL2 still shows a good PL, extending the RT emission wavelength to 1242 nm. Further addition of Sb and N leads to longer emission wavelengths, while the optical properties are progressively degraded. Nevertheless, this is partially due to the transition to a type-II band alignment, as evidenced by the PL peak blue-shift observed with excitation power in sample SL3 (inset in Fig. 7.12 (b)), which is typically attributed to the spatial separation of the photoexcited carriers [158]. This shows that the band alignment of InAs QDs can be tuned by controlling the Sb and N contents in the GaAsSb/GaAsN SL. Despite the type-II alignment, contrary to what is observed in the sample with the quaternary CL, RT PL is obtained even from sample SL3, emitting at 1426 nm. This means that longer emission wavelengths at RT are reachable

through this approach than those reported previously in Section 7.3.4 by using a quaternary GaAsSbN CL grown under optimized growth parameters.

Fig. 7.12: (a) 15 K PL spectra for samples GaAs, GaAsSbN, and SL. The inset shows the RT PL spectra for the three samples. (b) RT PL spectra for samples SL, SL2, and SL3. The inset shows the dependence of the PL peak energy on the third root of the excitation power for samples SL and SL3. The lines are linear fits to the data.

In order to analyze the structural changes introduced by using the GaAsSb/GaAsN superlattice CL and understand its benefits with respect to the quaternary CL, a study was carried out by AFM and TEM techniques. The structure of the buried QDs and CL was studied by X-TEM in samples GaAsSbN and SL3, which have a very similar wavelength at low temperature and therefore similar N and Sb contents. Fig. 7.13 (a) shows a g002 dark-field image of a region containing two QDs in sample GaAsSbN, where it can be observed that the QDs are not homogeneously covered by the CL and present clear differences in size and shape. This observed contrast on top of the QDs is probably due to strain effects induced by the accumulation of Sb in these regions when using a standard GaAsSbN quaternary CL, as it has already been found in similar samples by TEM [234] and X-STM [109]. Moreover, the presence of a few dislocations originating on top of the large QDs and propagating through the CL was also observed. The accumulation of Sb around the largest QDs could lead to a strong strain accumulation eventually favoring the formation of such defects, what could explain the absence of PL emission at RT. Fig. 7.13 (b) shows a histogram of the measured QD heights, compared with the height distribution of uncapped QDs obtained by AFM. While the height of the uncapped QDs fits a normal distribution, the height distribution of the buried QDs exhibits the presence of two height modes, as shown in Section 7.3.3.4. As mentioned in Section 7.3.3.4, this may be a result of the inhomogeneous covering

of the QDs during the simultaneous deposition of N and Sb [234], whereby Sb would accumulate to a higher degree on top of the large QDs, preventing them from decomposition [108]. This model is in good agreement with the fact that dislocations were found to originate only on top of larger-size QDs.

Regarding sample SL3, a CL homogeneously covering the QDs was found without the presence of any kind of defect surrounding the QD or inside the CL region (Fig. 7.13 (c)). Though the superlattice period is too small to be observed using dark-field contrast diffraction TEM mode at the magnifications used in this study (50-100K), a more homogeneous contrast is appreciated within the CL, indicating that this deposition procedure induces a more homogeneous growth. Moreover, the histogram of the measured QD heights (Fig. 7.13 (d)) shows a distribution that fits a normally distributed population with an average QD height of 4.7 ± 0.7 nm. Thus, the growth of the superlattice CL on top of the QDs leads to the formation of a single QD height population with a reduced standard deviation. This is contrary to what happened to GaAsSbN-capped QDs, where the CL inhomogeneity was likely responsible for the bimodal distribution.

Fig. 7.13: g002 dark-field X-TEM images of samples GaAsSbN (a) and SL3 (c). A dislocation originating on top of a QD is observed in GaAsSbN. (b) and (d) show the measured QD height distribution in samples GaAsSbN and SL3, respectively, together with that of the surface QDs measured by AFM. Normal curves are superimposed on the pertinent histograms.

HR-TEM image analysis was also performed in samples GaAsSbN and SL3. The Sb content was estimated by EDX spectroscopy to be $17.4 \pm 2.6\%$ and $17.9 \pm 3.1\%$, respectively, agreeing quite well with the nominal values (note that an average content for the whole CL is determined, which in SL3 should be half the nominal value). This overall Sb content above 16% should result in a type-II band alignment, in agreement with the results from PL vs.

excitation power shown previously for SL3. Once the Sb content is known, the amount of N in each CL can be estimated from strain analysis. Thus, strain maps of the CL were obtained from HRHAADF images acquired on the [110] pole axis using geometrical phase analysis [249]. Two representative strain maps of a QD in samples GaAsSbN and SL3 are shown in Fig. 7.14. In the CL of SL3 an overall compressive strain is observed instead of a superlattice-like structure with alternating regions of compressive and tensile strain. This is likely due to Sb-N intermixing at the GaAsSb-GaAsN interfaces, which for the nominal Sb/N ratio would lead to compressive strain. The average CL-GaAs misfit along the growth direction far from any QD was determined to be $1.74 \pm 0.08\%$ in sample GaAsSbN and $1.48 \pm 0.06\%$ in sample SL3. From these strain values, N contents of 2.2 ± 0.3 (sample GaAsSbN) and 3.1 ± 0.3 (sample SL3) are deduced assuming Vegard's law [234].

Fig. 7.14: Strain maps obtained from HRHAADF images acquired along the [110] pole axis for a region containing a QD in samples GaAsSbN (a) and SL3 (b).

The height of the representative QD is 6 nm for sample GaAsSbN, belonging to the higher-size population, and 5.4 nm for sample SL3. Stronger fluctuations in the strain fields are found in the CL of sample GaAsSbN, as a consequence of compositional inhomogeneities, leading to an irregular growth front profile. In addition, the compressive strain is strongly intensified in the immediate QD-surrounding space region in agreement with the expected accumulation of Sb. This occurs to such a degree that the CL on top of the QD can hardly be distinguished from the dot in the strain map image. By contrast, a more homogeneous strain field is observed inside the superlattice-CL structure, where the QD-CL interface can be now quite well identified. Despite the higher Sb and N content in the superlattice CL, a more regular CL-GaAs interface is found in this case, the growth front being flat even on top of the QD. Therefore, the QD is in this case homogeneously covered by the CL, supporting our previous conclusions that Sb and N are being more homogeneously distributed in the CL. Hence, it appears evident that the N-related enhancement of the GaAsSb

immiscibility [234] is somehow avoided by intentionally separating both ternary phases during the CL deposition.

The previous analysis shows that the improved optical properties observed when using the superlattice CL are directly related to the better structural characteristics obtained by avoiding the simultaneous presence of Sb and N on the growth surface. Separating Sb and N in a short-period superlattice-like structure reduces mass transport phenomena and results in a more homogeneous CL with suppressed composition modulation. Moreover, the reduced Sb accumulation around the QDs avoids excessive strain accumulation, reducing defect formation and giving rise to a narrower QD height distribution. All this allows reaching RT PL emission at long wavelengths which are unattainable with a conventional GaAsSbN CL. Therefore, this approach could allow exploiting the complementary advantages of Sb and N-containing CLs in GaAs-based devices working at RT.

As a device demonstration, a sample was grown in which the active region of sample SL2 was embedded in a p-i-n junction and subsequently processed as described in Section 3.4. RT PC at 0 V is shown in Fig. 7.15, together with RT cw EL at 0.6 A/cm². The EL peak at 1262 nm matches quite well the first shoulder observed in the PC so this absorption edge can be attributed to the QD ground state. The strong lower-wavelength PC absorption edge at around 1000 nm is likely related to the CL. This means that this structure could also work as a hybrid QD-QW solar cell. Remarkably, the PC induced by the QD ground state absorption appears to be significant taking into account that this current is generated from a single QD layer. These preliminary results suggest the possibility for stacking QD layers in order to significantly enhance QD solar cell efficiencies around 1 eV using both Sb and N in the CL.

The external quantum efficiency (η_{ext}) of the device used as a light emitting diode (LED) was determined and represented together with those of GaAsSb-, InGaAs- and InGaAsN-CL devices with the same epitaxial structure and fabrication procedure (inset of Fig. 7.15). The value of η_{ext} is comparable to that of GaAsSb-capped InAs QD devices emitting at similar wavelengths [250]. Moreover, η_{ext} is three orders of magnitude larger than in previously reported LEDs with a N-containing CL [251]. This is a good indication of how the superlattice CL structure can be used to produce efficient light emitting devices with increased degrees of freedom regarding band structure engineering.

Fig. 7.15: PC at 0 V and EL at 0.6 A/cm² spectra for the processed p-i-n sample containing a similar active region to that of sample S-SL2. The inset shows the external quantum efficiency of the SL-CL LED together with that of similar LEDs containing GaAsSb-, InGaAs- and InGaAsN-CLs.

7.4. Conclusions

The effect of modifying the growth conditions of the quaternary GaAsSbN CL on the PL properties of the InAs/GaAs QDs has been analyzed. Regarding the growth temperature, 470 °C was found to be the optimum value. A clear tendency was found when modifying the CL thickness whereby the peak is red-shifted and the PL degraded as the CL thickness increases. The best results were found when increasing the CL growth rate. The strong PL improvement at high growth rates up to 2 MLs⁻¹ is shown to be specific for N-containing structures, and likely related to a reduced composition modulation and plasma ion-induced defect density. Nevertheless, an apparent limitation regarding N incorporation is found when growing the CL at 2 MLs⁻¹, which is avoided at 1.5 MLs⁻¹ allowing for the achievement of longer wavelength by increasing the active N flux. RT PL is obtained through different growth conditions, some of them leading to 1.3 μm emission. The best luminescence properties were found for the highest CL growth rate, being still possible to extend the emission wavelength by adding higher Sb contents.

It has been found that the growth rate of GaAsSbN CLs affects the final QD size, shape and distribution in a similar way as the capping rate of GaAs/InAs/GaAs QDs. The QD dissolution during capping in both GaAs- and GaAsSbN-capped InAs QDs seems to be governed by a kinetically limited surface diffusion process.

Regarding the use of a short-period GaAsSb/GaAsN superlattice CL after the InAs QD growth, it leads to a more homogeneous CL compared to the case of the quaternary GaAsSbN, with reduced clustering and uniform and abrupt QD-CL and CL-GaAs interfaces. Moreover, it avoids Sb accumulation around the QDs and the consequent origination of extended defects, resulting also in a narrower QD height distribution. This all entails a significant PL improvement allowing the incorporation of high N contents and the achievement of RT emission beyond 1.4 μm . Moreover, we demonstrate that this approach can be used in efficient photodetectors and LEDs working at RT.

The outcomes obtained from the growth optimization of this system could represent a starting point from which the versatility of the GaAsSbN CL might be exploited for real device applications. In addition, the improvements achieved through the spatial separation of Sb and N, alternately introduced as a short-period superlattice, also suggest the possibility to replace bulk GaAsSbN with GaAsSb/GaAsN superlattices improving the alloy structural quality and suitability for different optoelectronic applications. Initial research on this issue will be addressed in appendix A.

8.1. Introduction

Once the growth of the GaAs(Sb)(N) CLs on InAs QDs is optimized, next objective is the implementation of such a system in the active region of p-i-n junction devices for solar cells. QD solar cells are expected to benefit from both the versatility of the QD-CL band structure and the ability to strain compensation in GaAsSbN-capped InAs QDs. Indeed, the addition of N to Sb-containing CLs should reduce the accumulated strain while tuning the electron confinement in the QD, allowing the combination of strain-balancing techniques with band-structure engineering in QD solar cells. A suitable ratio of Sb to N in the CL would compensate the accumulated strain allowing a higher number of stacked QD layers before relaxation via origination of extended defects. This is also expected to mitigate the loss in V_{oc} induced by the presence of InAs QDs, as found through different strain-balancing techniques [226–228]. Moreover, the absorption edge would be additionally shifted to longer wavelengths due to the reduced conduction band offset, absorbing a broader region of the solar spectrum and increasing the I_{sc} .

8.2. Sample description

A series of p-i-n junction solar cells were grown whose active region (Fig. 8.1) consists of ten InAs QD layers grown by depositing 2.8 MLs at $\sim 0.04 \text{ ML s}^{-1}$. The different CL materials, described below, were always deposited at 470°C , immediately followed by a 10 ML-thick LT GaAs layer to avoid Sb/N desorption. Subsequently, 35 nm-thick GaAs spacers were grown at 580°C in order to avoid the formation of extended defects [217,218]. Due to the comparative nature of this study, a simple device structure was chosen so no window layer or antireflection coating was used (parameters such as the doping levels or the emitter and intrinsic region thicknesses are not either optimized). The whole active region was sandwiched in the middle of a 400 nm-thick intrinsic GaAs layer, grown on a 500 nm-thick n-GaAs base buffer and ended in a 350/150 nm-thick p-/p⁺-GaAs layer. Mesa-processed solar cell devices with 200 μm diameter were finally fabricated following the procedure described in Section 3.4.

Fig. 8.1: Sketch of the solar cells containing ten stacked InAs QD layers capped with a thin GaAs(Sb)(N) CL.

8.3. Results and discussion

The initial comparative analysis was carried out using 5 nm-thick GaAsSbN and GaAsN CLs (samples S-SbN and S-N, respectively). A 2MLs^{-1} growth rate, particularly beneficial for N-containing samples [252], as shown in Chapter 7, was used for the growth of the CL in all these samples. The Sb and N nominal contents were always set to 10 and 2.0%, respectively. In addition, samples S-Sb_I (with the same nominal Sb content as S-SbN), S-0, and the reference GaAs (with no QDs inside) from Chapter 6 are used for comparison.

8.3.1. Structural analysis and photoluminescence

g002 Dark-field X-TEM images in Fig. 8.2 (a) show global views of the ten QD layers in samples S-0, S-Sb_I, S-N, and S-SbN (from left to right, respectively). The period thickness in both S-N and S-SbN were found to be approximately 40 nm, close to the expected value

(TEM-measured periods were 40 and 50 nm in sample S-Sb_I and S-0, respectively). A representative QD, from each sample, has now been zoomed in for more detail (Fig. 8.2 (b)), clearly highlighting the brighter contrast in both Sb-containing CLs. The CL-GaAs interface appears well defined, with the CL covering homogeneously the QDs in all cases. This indicates that composition modulation in the CL is suppressed to high extent even in the case of the quaternary alloy, likely due to the beneficial impact of the high growth rates. No extended defects are observed. Similar constant thicknesses were estimated for S-N and S-SbN (approximately 5.5 nm), near the nominal thickness. For the sake of clarity, a sketch of the expected QD-CL band structure for a single layer in each sample is also represented in Fig. 8.2 (c).

Fig. 8.2: (a) g002 Dark-field X-TEM image from samples S-0, S-Sb_I, S-N, and S-SbN from left to right. (b) Zoom of one representative QD and (c) sketch of the expected band structure in each sample.

Fig. 8.3: (a) θ -2 θ XRD scans around the (004) Bragg reflection performed on samples S-0, S-Sb_I, S-N, and S-SbN, showing that the increasing accumulated strain is directly correlated with the PL FWHM (b).

Fig. 8.3 (a) shows high resolution XRD θ -2 θ scans around the (004) reflection as a function of the CL material. The presence of abrupt heterointerfaces with an exceptionally high periodicity throughout the superlattice structure also results in the clearly observed satellite peaks in the N-containing samples. Period thicknesses of 41 and 40 nm are obtained for S-N, and S-SbN, respectively, in good agreement with those estimated by TEM (XRD-measured periods were 40 and 48 nm in sample S-Sb_I and S-0, respectively). The average strain induced by the introduction of InAs QDs into the GaAs host material is partially compensated by applying a GaAsN CL, as the smaller shift of the zeroth order satellite peak with respect to the substrate Bragg angle indicates. Thus, the GaAsN CL is acting as a strain-compensating layer [124,230]. In addition, as observed in Fig. 8.3 (a), the higher accumulated strain observed in S-Sb_I is also relatively compensated by the addition of N in the CL. However, there is still an accumulation of compressive strain with respect to sample S-0, due to the fact that the Sb/N ratio ($\approx 10/2$) is higher than that for lattice-matching condition ($\approx 10/4$) [239]. The normalized PL spectra from this series of samples (Fig. 8.3 (b)), depicted together to each respective rocking curve, reveal again a direct correlation between the PL FWHM and the accumulated strain. The addition of N to GaAs and GaAsSb CLs reduces

the PL FWHM, which clearly increases monotonically with the accumulated strain, regardless of the CL material and emission wavelength. Regarding the PL peak energies, the shifts with respect to the reference sample are 64, 93, and 163 meV for S-N, S-Sb_I, and S-SbN, respectively. The energy shift for sample S-SbN is therefore approximately the same as the one resulting from the addition of those in samples S-Sb_I and S-N. This confirms that the effect of Sb and N on the band structure is cumulative (see Fig. 8.2 (c)), and, therefore, the electron and hole confinements can be independently tuned in stacked QD layers.

8.3.2. Effect of the N incorporation on carrier collection and solar cell performance

Fig. 8.4 (a) shows the J-V characteristics under AM1.5D illumination for samples S-0 and S-SbN together with that of the GaAs control sample. As observed, the addition of N to the GaAsSb CL leads to a drastic reduction in J_{sc} , despite the N-related reduction of the accumulated strain and the reduced PL FWHM shown in the previous section. The physical mechanisms involved in the drastic J_{sc} drop in the N-containing devices are analyzed below.

Fig. 8.4: (a) J-V characteristics of the sample S-SbN, together with that of the GaAs reference sample and S-0, for comparison, under 900 W/m² AM1.5D conditions. (b) RT PC spectra from samples S-N and S-SbN together with that from S-0 for comparison.

RT PC from samples S-N and S-SbN are shown in Fig. 8.4 (b) together with that of sample S-0 for comparison. As expected, the use of a GaAsN CL extends the photoresponse beyond that of sample S-0, where the contribution of the QD ground state and the CL is clearly observed. However, PC originating from the GaAs layers is now significantly reduced. This is also observed in sample S-SbN, in which there is a weaker contribution from the QD-CL structure to the PC. Although N is reducing the accumulated strain, the addition

of N yields a degradation of the GaAs contribution to the total PC, giving rise to the observed drastic drop in J_{sc} .

Fig. 8.5: (a) I-V curves from the GaAs reference sample, S-Sb_I, S-N, and S-SbN, under 1.46 eV illumination. (b) Conductance as a function of the voltage in samples S-N and S-SbN under 1.37 eV illumination.

The strongly hindered carrier collection of the carriers photogenerated in GaAs can be now observed from I-V measurements conducted under 1.46 eV monochromatic illumination, over the GaAs band gap energy. Fig. 8.5 (a) shows the monochromatic I-V curves from the GaAs reference sample, S-Sb_I, S-N, and S-SbN. Reverse biases up to -4V were applied. The measurements show the increase of the photogenerated current with the applied reverse bias in N-containing samples due to the incomplete carrier collection [223]. The nearly constant value of the PC with voltage in sample S-Sb_I confirms that the GaAsSb CL is hardly affecting carrier transport, as discussed in Chapter 6, but for low biases. The situation is utterly different in N-containing samples, where a strong dependence of the current on the applied bias is observed. Despite being much lower at 0 V, the PC from sample S-N merges with that from S-Sb_I and the reference sample at a bias close to -4V. This points to the fact that the GaAsN CLs are significantly limiting the collection of the photogenerated carriers at low biases, likely as a result of an electron-trapping mechanism. In the case of sample S-SbN, increasing the reverse bias does not yield a total PC comparable to that from the other samples. Hence, some additional carrier loss mechanism must be present, such as recombination at point defects that may be generated by the simultaneous presence of Sb and N. Moreover, the addition of N to GaAsSb makes the quaternary CL in the region between QDs behave as a QW with a type-I band alignment (GaAsSbN/InAs/GaAs). This implies a radiative recombination faster than in the structures with the ternary CLs, acting as type-II GaAsSb/InAs/GaAs and GaAsN/InAs/GaAs QWs, which could also explain the degraded carrier extraction efficiency observed in this sample.

Illuminating with light below the GaAs band gap energy, most carriers are generated inside the nanostructures. Under such conditions, a possible hindered extraction of the photogenerated carriers is added to retrapping effects. Indeed, the conductance in samples S-N and S-SbN (Fig. 8.5 (b)), calculated as the first derivative of their I-V curves, shows an oscillatory behavior with the applied bias, not present in sample S-Sb_I. This suggests the presence of a resonant Fowler-Nordheim tunneling component, resulting from the accumulation of negative charge in the CLs [222,253]. As shown in Fig. 8.6, this accumulation of negative charge reduces the depletion region within the intrinsic layer so that those CLs with accumulated charge remain outside the depletion region. The application of an increasing reverse bias enhances electron escape, progressively releasing trapped electrons from the CLs closer to the onset of the depletion region. Hence, this released accumulated charge sequentially contributes to the net drift current. This mechanism must be caused, in its turn, by a significant difference between the electron and hole escape times, whereby holes escape much faster so that electrons cannot recombine. In addition, this accumulation of negative charge also suggests a presumed accumulation inside the QD, what could be increasing Coulombian scattering through a higher density of confined carriers [254].

Fig. 8.6: Schematic illustration of the conduction band with N-containing CLs in the intrinsic region and the accumulation of electrons in those CLs closer to the p-region. Electrons are sequentially released by the application of higher reverse bias.

Fig. 8.7 shows the PC spectra at 0 V and -3 V from samples S-Sb_I and S-N. PC from sample S-Sb_I shows a slight increase over the whole spectrum range when applying the reverse bias, as already discussed in Section 6.3.3, while that from sample S-N undergoes such a strong increase that PC originating from GaAs is now as high as that in S-Sb_I sample. Remarkably, the contribution of the QD-CL structure is now significantly higher than that of S-Sb_I, contrary to what happens at 0 V. Two conclusions can be drawn from these results:

- The QD-CL system in sample S-N is absorbing more efficiently than in sample S-Sb, but carriers cannot be extracted except for high reverse applied bias.
- The collection of photogenerated carriers is hindered by retrapping in the N-containing CLs, as deduced from the Fowler-Nordheim escape mechanism. This means that the reduced PC at 0 V in S-N is not only due to the possible presence of N-induced point defects. Moreover, this would now fit with a positive impact of strain reduction in the structure, which was hidden by reduced collection efficiency at 0 V. Hence, it may be possible to further exploit such a structure through the optimization of the built-in electric field for a more efficient extraction at operation voltages.

Fig. 8.7: RT PC spectra from samples S-N and S-Sb_I at 0 V and -3 V bias.

8.3.3. Carrier escape times: theoretical modelling

According to the optical and optoelectronic properties, the structural quality in the sample with a GaAsN CL is now beyond question and a hindered carrier extraction from the nanostructures and retrapping of carriers photogenerated in GaAs are considered the main reasons for such a reduced carrier collection in S-N sample. The addition of 2%N contents in the CL lowers the conduction band far below the InAs WL ground state forming a deep QW. Hence, the impact of the WL seems to be negligible in this case, so that the higher radiative lifetime due to the type-II structure may not be sufficient to outweigh the long escape times for such a deep QW.

In order to theoretically assess the carrier escape times from such structures, the energy levels in these QWs were calculated solving a one-dimensional Schrödinger equation

through a finite-differences method. With the aim of simplifying the analysis, the WL was not considered now in the simulations, since the QW depth is most probably dominant. A GaAsSb QW equivalent to the CL of S-Sb_I was also simulated without considering the WL, in order to compare the expected escape times from both kinds of structures. The thickness of the QWs was taken to be 5.5 nm, as found by TEM, whereas the nominal Sb and N contents, i.e., 10 and 2%, respectively, were used. Regarding the GaAsSb QWs, the band gap energy and band offsets were estimated at RT from experimental results for GaAsSb pseudomorphically grown on GaAs [197], while the hole effective mass is obtained from a linear interpolation between the binaries. As for the GaAsN QWs, the band gap energy and band offsets were considered as predicted by the BAC in first order perturbation theory [255], with the specific values for the electron effective mass and BAC parameters as described in Ref. [256]. The results from the simulations are depicted in Fig. 8.8. Three confined levels were found for the GaAsSb QWs, with an escape barrier of 164 meV for the ground state. For the case of GaAsN QWs, two energy levels were obtained, the barrier for the ground state being 291 meV. Once the confined energy levels are known for the QWs, the thermal carrier escape times τ_{th} can be estimated, given by [257]:

$$\frac{1}{\tau_{th}} = \frac{1}{L_w} \sqrt{\frac{k_B T}{2\pi m^*}} \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (6.1)$$

where L_w is the width of the QW, m^* is the carrier effective mass inside QW, k_B is Boltzmann constant, T is temperature, and ΔE is the barrier height. With this expression, the RT thermal escape time from the ground state for holes in the GaAsSb QW and electrons in the GaAsN QW are estimated to be approximately 0.08 and 6 ns, respectively. Thus, the electron escape time is around two orders of magnitude longer than that of holes. This is in agreement with the experimental results in the previous section, supporting the hypothesis that electron trapping and hindered extraction are responsible for carrier collection losses in the N-containing samples. Under no applied field, tunneling escape time is negligible and the high electron escape time leads to an accumulation of negative charge giving rise to the formation of high-field domains in the N-containing QWs [253]. This leads to a sequential Fowler-Nordheim tunneling mechanism with the application of a reverse bias, which is superimposed to the thermal escape component being responsible for the observed oscillations in the current derivative curves with the applied voltage (Fig. 8.5 (b)). Regarding sample S-SbN, the type-I band structure, which is just the addition of the two shown in Fig. 8.8, involves faster radiative recombination rates inside the CL, further hindering carrier extraction. This, together with an additional loss mechanism likely due to non-radiative recombination at point defects, results in a strongly degraded solar cell performance in the case of the quaternary CL.

Fig. 8.8: Results from finite-differences method simulations for confined energy states and carrier escape times in GaAsSb/GaAs and GaAsN/GaAs QWs.

8.3.4. Alternative approaches for the quaternary capping layers

In an effort to obtain improved characteristics using the quaternary CL, alternative structures containing simultaneously Sb and N were designed. The other two successful growth approaches for the quaternary CL shown in Chapter 7 were used, namely, a thin CL [252] and a superlattice-like CL [183]. Two new samples were fabricated following the same procedure described in Section 8.2. The former structure consists of a 2.5 nm-thick quaternary GaAsSbN CL (sample S-thin), which was shown to result in a strongly enhanced PL emission (Fig. 7.4). Moreover, in this structure a mitigation of carrier retrapping and a more efficient extraction from the thinner QW (due to reduced localization energy) are expected. The latter one consists of a short-period superlattice CL containing 5 periods of GaAsSb(2ML)/GaAsN(2ML) (sample S-SL), which was also found to give rise to an improved structural quality of the CL as compared to the standard GaAsSbN alloy. Both CLs were grown under the same conditions for the Sb and N sources.

Fig. 8.9 (a) shows I-V measurements under 1.46 eV monochromatic illumination, offering a first insight into the impact of the modified CL structures on carrier transport. Unlike the sample with the standard quaternary CL (S-SbN), the thin and short-period superlattice approaches allow achieving a complete carrier collection at negative voltage. A reduction of the point defect density through the improved CL material in S-SL and the expected mitigation of carrier retrapping and more efficient extraction from the thinner QW in S-thin must be behind the improved carrier collection with reverse bias. As observed in Fig. 8.9 (b), the improved carrier collection leads to significant J_{sc} increases of 19% in S-SL and of 49% in S-thin with a difference in V_{oc} within the 2% in both cases.

Fig. 8.9: (a) I-V curves from the GaAs reference sample, S-thin, S-SL, and S-SbN, under 1.46 eV illumination. (b) J-V characteristics of samples S-thin, S-SL, and S-SbN under 900 W/m^2 AM1.5D conditions.

Fig. 8.10 (a) shows the PC at 0 V of samples S-thin, S-SL and S-SbN. The beneficial impact of both alternative approaches is reflected in an enhanced PC over the whole range of absorption. Strongly improved PC is particularly observed from the QDs and CL, highly contributing to the improved J_{sc} . The PC at -3 V reverse bias corresponding to these three samples are shown in Fig. 8.10 (b) together with that from S-0 for comparison. As observed, at negative bias, all samples undergo significant PC enhancements. Indeed, in samples S-thin and S-SL, the PC contribution from GaAs becomes close to that of sample S-0, in agreement with the monochromatic I-V curves. Remarkably, the QD-CL-generated PC exceeds to a great extent the contribution of the structures with the sole presence of InAs QDs capped with GaAs.

Fig. 8.10: (a) RT PC spectra at 0 V from samples S-SbN, S-thin and S-SL. (b) RT PC spectra at -3 V from S-0, S-SbN, S-thin, and S-SL.

8.3.5. Analysis of relative contributions to the total photocurrent: Impact of the capping layer nature

The contribution of the PC from GaAs and the QD-CL structure has also been evaluated in the N-containing samples by integrating in the respective range of wavelengths at 0 and -3 V applied biases, as described in Section 6.3.3. The estimations are summarized in Table 8.1, showing PC_{GaAs} and PC_{QD-CL} from all of the N-containing samples, together with those values from the GaAs reference sample, S-0, S-Sb_I, and S-Sb_{II} (all the solar cell devices analyzed in this thesis). The main conclusions drawn from the values in Table 8.1 are the following:

- Despite the strong reduction of PC_{GaAs} in N-containing samples, PC_{QD-CL} at 0 V from S-N exceeds that from S-0, while PC_{QD-CL} from S-thin and S-SL are comparable to it.
- S-N, S-thin and S-SL undergo a very significant enhancement in the integrated PC under -3 V reverse bias as compared to short-circuit conditions. Particularly, an essentially complete carrier collection is now achieved in sample S-N, revealed from the value of PC_{GaAs} , approximately 1. Although this value is not reached in the other N-containing samples, all of them show a very significant increase not only in PC_{GaAs} , but also in PC_{QD-CL} .
- The fact that PC_{GaAs} approaches the saturation value at -3 V and reaches it at some higher negative biases (see Fig. 8.9 (a)) in samples S-thin and S-SL, reveals that extraction problems are now related to the type-I structure of the QWs rather than to the presence of defects. Therefore, this drawback could in principle be overcome by a stronger electric field in the intrinsic region.
- Samples S-N, S-thin, and S-SL, were found to show a PC_{QD-CL} much higher than S-0 at -3 V. Indeed, the values for PC_{QD-CL} of S-N and S-SL exceed even that of S-Sb_{II}. The reduced accumulated strain in these structures as compared to Sb containing samples could therefore be playing a positive role in the PC. Such N-containing structures are therefore good candidates to achieve enhanced photoresponse and significantly exceed the value of J_{sc} for standard GaAs solar cells if transport problems are solved through an optimized solar cell design.

	PC _{GaAs}		PC _{QD-CL}	
	0 V	-3 V	0 V	-3 V
GaAs	1	1	---	---
S-0	0.94	1.14	0.13	0.21
S-Sb _I	1	1.13	0.31	0.38
S-Sb _{II}	0.84	1.10	0.47	0.62
S-N	0.26	1.04	0.15	0.65
S-SbN	0.17	0.29	0.01	0.35
S-thin	0.23	0.69	0.11	0.54
S-SL	0.21	0.63	0.11	0.73

Table 8.1: Estimation of the integrated PC between 1.37 and 1.6 eV (PC_{GaAs}), related to the GaAs absorption, and for energies under 1.37 eV (PC_{QD-CL}), corresponding to the contribution from the nanostructures (QD-CL).

8.4. Conclusions

In conclusion, the use of N in GaAs(Sb) CLs for InAs QD solar cells has been demonstrated to allow the compensation of the accumulated strain, not only in a ternary GaAsN CL, but also in the quaternary GaAsSbN CL. This makes it possible to stack a higher number of QD layers before the origination of extended defects. In addition, the use of N in the CL has also been found to extend the photoresponse of a QD solar cell, further extending it in combination with Sb through an independent control of the conduction and valence bands. However, the use of N-containing CLs leads to a strong reduction in J_{sc} , which is explained in terms of hindered electron extraction and retrapping in the N-containing CLs. The observed escape of electrons by way of a resonant Fowler-Nordheim tunneling mechanism points in this direction. Indeed, the CL potential depth, thickness, and the structure growth procedure, as well as the structure band alignment, have been found to play an important role in carrier extraction and transport, pointing to the fact that there is still room for optimization of these QD-CL structures leading to more efficient devices.

9 Conclusions

The main achievements and conclusions in the framework of this thesis are described in this section, broken down according to the CL/QD system under study, as the main manuscript is divided.

9.1. GaAs/InAs/GaAs quantum dots

A straightforward approach has been proposed aimed at limiting the ever-observed dissolution of GaAs/InAs/GaAs QDs during the capping process and increase the degree of freedom when seeking to tune the QD morphology without altering the band structure. Two main achievements have been reached in this regard:

- Control over the final size and ground state energy of standard GaAs/InAs/GaAs QDs by means of the capping rate, achieving the complete QD preservation and suppressed decomposition for capping rates above $\sim 2\text{MLs}^{-1}$.
- Control over the WL thickness by means of the capping rate, achieving a significant reduction of the WL thickness for higher capping rates as a consequence of the kinetically limited diffusion of In atoms from the QDs to the regions in-between them.

9.2. GaAsSb/InAs/GaAs quantum dots

The use of thin GaAsSb CLs in both QD LDs and solar cells has been analyzed. The use of different Sb contents allowed analyzing not only the ability to control the emission-absorption wavelength of operation, but also the impact of the QD-CL band alignment in the performance of both QD LDs and solar cells. The application of such CLs additionally helped further understand the impact of QDs and WL on carrier transport. The following are the main achievements and conclusions:

Lasers

- Ability to extend the lasing wavelength of GaAsSb/InAs/GaAs QD LDs with the Sb content in the CL, although by means of excited states.
- Strongly reduced J_{th} in GaAsSb/InAs/GaAs QD LDs with Sb contents within both type-I and type-II QD-CL band-alignment regimes.

- Substantially improved η_d in type-I GaAsSb/InAs/GaAs QD LDs, likely due to improved carrier injection efficiency.
- Improved thermal stability in type-II GaAsSb/InAs/GaAs QD LDs, likely due to the higher barrier for holes, which are already confined in the CL.

Solar cells

- Ability to extend the absorption edge of GaAsSb/InAs/GaAs QD solar cells with the Sb content in the CL, achieving photoresponse up to beyond 1.5 μm with a type-II QD-CL band alignment.
- Hybrid QD-QW solar-cell operation due to the strong additional contribution to the PC from the CL, which acts itself as a QW.
- Improved carrier collection efficiency in GaAsSb/InAs/GaAs QD solar cells as compared to InAs/GaAs QD solar cells, likely due to the type-II WL-CL band alignment. Indeed, the WL-CL band alignment was found to exert a higher impact on the performance of a GaAsSb/InAs/GaAs QD solar cell than the QD-CL band alignment under 1 sun illumination.
- Efficiency improvements up to 20%, as compared to the reference QD solar cell, with the application of a GaAsSb CL using a moderate Sb content ($\sim 10\%$). Although higher Sb contents ($\sim 20\%$) leads to a larger contribution from the nanostructures to the PC in GaAsSb/InAs/GaAs QD solar cells, a lower improvement of 10% is achieved, most likely due to the presence of dislocations following the excessive accumulated strain.
- Significantly faster V_{oc} increase under light concentration in type-II GaAsSb/InAs/GaAs QD solar cells induced by a faster quasi-Fermi-level splitting with injection current, achieving an V_{oc} even higher than the effective band gap. The type-II band alignment appears as a competing factor in GaAsSb/InAs/GaAs QD solar cells not only in the QD-CL, but also in the WL-CL structure, allowing an enhanced improvement of the V_{oc} under light concentration. This leads to V_{oc} exceeding that of the reference QD solar cell with Sb contents in the CL within both type-I and type-II QD-CL band-alignment regimes.

9.3. GaAsSbN/InAs/GaAs quantum dots

Before applying the versatile GaAsSbN CL to any QD-based device, the main goal was the optimization of its growth conditions on InAs QDs. Once optimized, the application of such a CL to novel QD LEDs and solar cells was studied. The following are the most relevant achievements and conclusions:

Growth optimization

- The growth temperature of quaternary GaAsSbN CLs on InAs/GaAs QDs was optimized. No significant effect on the PL peak energy was found in the range 450 – 480 °C, while the growth of the CL at ~ 470°C led to the best PL properties.
- A reduced thickness of GaAsSbN CLs was found to improve the PL properties, blue-shifting the PL peak energy though. This approach allowed achieving RT PL at 1250 nm.
- The growth rate of GaAsSbN CLs was shown to have a strong impact on the PL properties of GaAsSbN/InAs/GaAs QDs. Higher growth rates lead to strong PL improvements not only in quaternary GaAsSbN CLs, but also in ternary GaAsN CLs, likely related to a reduced composition modulation and plasma ion-induced defect density. RT PL beyond 1.3 μm from GaAsSbN/InAs/GaAs QDs was achieved through this approach. However, higher growth rates entail a strict limitation regarding N incorporation in GaAsSbN CLs.
- The growth rate of GaAsSbN CLs affects the final QD size and shape and their distribution in a similar way as the capping rate of GaAs/InAs/GaAs QDs does, so that the QD dissolution during capping is also ultimately governed in this case by a limited surface diffusion process controlled by the overgrowth kinetics.
- The use of ultrashort-period GaAsSb/GaAsN instead of bulk GaAsSbN on InAs/GaAs QDs leads to a more homogeneous CL, with reduced clustering and uniform and abrupt QD-CL and CL-GaAs interfaces, avoiding the accumulation of Sb around the QDs and the consequent origination of extended defects.
- GaAsSb/GaAsN ultrashort-period superlattice CLs on InAs/GaAs QDs allowed improving the PL properties, allowing the incorporation of high N contents and achieving RT emission beyond 1.4 μm . The application of this approach allowed for the achievement of a much higher quantum efficiency in a test GaAsSb/GaAsN-capped InAs/GaAs QD LED working at RT close to 1.3 μm than in similar LEDs capped with InGaAs(N) layers.

Solar cells

- The addition of N in GaAs(Sb)/InAs/GaAs QD solar cells allows for the compensation of the accumulated strain, which allows increasing the number of stacked QD layers while avoiding the origination of extended defects.
- The addition of N in GaAs(Sb)/InAs/GaAs QD solar cells allows further extending the photoresponse through an independent control of the conduction and valence bands in combination with Sb. However, the addition of N leads to a strong reduction in J_{sc} , which is explained in terms of hindered electron extraction and retrapping in the N-containing CLs.
- The use of alternative GaAsSbN CLs, such as thinner or superlattice-like CLs, allows improving the performance of GaAsSbN/InAs/GaAs QD solar cells, pointing out to the fact that there is still room for optimization of such structures leading to more efficient devices.

10 Future work

The results obtained and presented in this thesis suggest some guidelines to follow in order to more deeply understand the mechanisms involved in the performance of QD LDs and solar cells and improve them. Some ideas already planned or even in process to follow are described below:

Lasers

- The design of GaAsSb/InAs/GaAs QD LDs enhancing gain from the QD ground state in order to achieve longer lasing wavelengths from both type-I and type-II structures. This could be possible by increasing QD density, stacking a higher number of QD layers, or using longer resonant cavities.
- If lasing from type-II transitions is achieved, analysis of the impact of the type-II band alignment on lasing characteristics. This would be, as far as we know, the first demonstration of a QD laser based on indirect transitions.
- The design of GaAsN/InAs/GaAs and GaAsSbN/InAs/GaAs QD LDs growing the N-containing CLs under optimized conditions. The significant improvement of such structures by the growth of the CL at high rates and the strong trapping-effect of N-containing CLs (detrimental in solar cells) could be exploited in order to achieve efficient carrier injection into the QDs and, therefore, efficient QD lasers emitting at longer wavelengths.

Solar cells

- The design of solar cells based on GaAsSb/InAs/GaAs QDs showing a type-II band alignment, with a moderate Sb content ~16-17%. This will allow analyzing and comparing the beneficial impact of type-II QD-CL structures while reducing the accumulation of strain and generation of extended defects, avoiding their impact on the device performance.
- The use of a residual amount of N throughout the spacer layer, in order to minimize its possible impact on V_{oc} , is also planned as an alternative to compensate the overall accumulated strain in Sb-containing QD solar cells while avoiding carrier trapping.
- The use of N-doped delta layers is an attractive alternative considered in case the previous approach might induce a negative effect on the V_{oc} . The use of periodic ultrathin GaAsN layers, inserted within the spacer layer, could be employed in an

attempt to reduce the accumulated strain without affecting carrier transport, due to the absence of confined states.

- The design of solar cells based on electronically coupled GaAsSbN/InAs/GaAs structures, by reducing the spacer layer thickness. In this case, minibands are formed from both the QD and CL electronic states, allowing for a long-range carrier transport through the active region. The improved carrier transport could help reduce carrier losses, improving the performance of the solar cell.
- Detailed analysis of the role of the WL in the performance of a QD solar cell. To do that, solar cells equivalent to those based on InAs QDs, but containing only WLs with different thickness below the critical thickness (to avoid the formation of QDs) have already been grown and processed. The analysis of these devices will allow retrieving direct information not only on the impact of the WL on carrier transport, but also on their role in carrier injection inside the QDs.
- The analysis on the impact of the WL can be complemented by using a thin GaAsSb CL on a thick WL. The use of such type-II structure, in the absence of QDs, will fulfill two purposes. On one hand, the improved PC along with a facilitated carrier extraction due to the higher radiative lifetimes could enhance the performance of a standard GaAs solar cell. On the other hand, this approach will allow deeper understanding of the impact of the type-II WL-CL structure on carrier transport and recombination.
- Transfer of the capping-rate approach to solar cell devices. The use of higher capping rates in GaAs/InAs/GaAs QDs will reduce the WL thickness and therefore its impact on carrier transport and collection and on V_{oc} . This should improve the performance of a QD solar cell.

Novel approaches for solar cells

- Design of intermediate-band solar cells based on type-II (Al)GaAsSb(N)/InAs/GaAs QDs. The achievement of the two-step photon absorption process in intermediate-band solar cells requires long electron lifetime in the intermediate band, which depends strongly on the carrier recombination strength and thermal escape. While carrier recombination rates are reduced by the addition of Sb to the CL in contents leading to a type-II band alignment, the addition of Al would strongly increase the conduction band offset in the structure and, therefore, reduce thermal electron escape from the intermediate band. Hence, this approach is promising to further advance towards efficient intermediate-band solar cells.

- Transfer of the superlattice approach to multi-junction solar cell technology. The use of subcells with an optimum band gap within the range 1-1.15 eV for triple- or quad-junction cells is one of the targets drawing most efforts in the field of solar cells. This band gap is easily reached by GaAsSbN while fulfilling lattice-matching condition to GaAs/Ge. This would also be possible by using GaAsSb/GaAsN SLs, which could improve the structural quality of the bulk quaternary and entail improved device performance. The initial work that we have done on this research line is shown in appendix A.

Appendices

A GaAsSb/GaAsN superlattices for optoelectronic applications

A.1. Introduction

Since they were first proposed for practical applications by L. Esaki and R. Tsu [258], semiconductor superlattice structures have found an increasing number of potential applications, sometimes arising as the key to overcome inconveniences inherent to standard bulk materials. The initial great interest in superlattices was raised by their suitability to achieve negative differential resistance for resonant tunneling diodes [259,260] and the possible amplification of electromagnetic waves [261] as condition for quantum cascade laser operation [262]. More recently, the family of strained type-II InAs/(In)GaSb superlattices has also drawn a huge interest in the field of long-wavelength infrared photodetection, due to the theoretically-estimated Auger lifetimes longer than those limiting the performance of HgCdTe-based devices in most applications. As another advantage of superlattice structures, we have also shown, in Section 7.3.5, the success achieved by the replacement of the standard GaAsSbN CL with a superlattice-like one in GaAsSbN/InAs/GaAs QDs. Indeed, this approach led to avoid the growth front corrugation induced by quaternary GaAsSbN CLs, yielding a more homogeneous strain-field surrounding the QD, without the presence of clusters or extended defects [183]. In addition, improved optoelectronic properties in both GaAsSbN/InAs/GaAs-based light emitting diodes and solar cells were also achieved [183,221]. This all suggests that the spatial separation of Sb and N in superlattice structures could avoid the growth problems in bulk GaAsSbN in order to fulfill the requirements in different cutting-off research fields. Indeed, like bulk GaAsSbN, such kind of superlattices are expected to allow for a huge versatility from the point of view of band gap and lattice parameter tunability, while avoiding the epitaxial growth problems related to the simultaneous addition of both Sb and N. The accomplishment of such expectations would make GaAsSb/GaAsN superlattices a suitable candidate for application in next-generation free-space optical communications or multi-junction solar cells. Indeed, on one hand GaAsSb/GaAsN superlattices could satisfy the lack of adequate material to produce uncooled highly efficient 1064 nm photodetection. On the other hand, their use for optimum 1-1.15 eV sub-cells in 3- and 4-junction cells [263,264], lattice-matched to GaAs/Ge, could represent an alternative to inverted metamorphic structures [265,266], avoiding the residual presence of extended defects, or to wafer-bonding [267] and mechanical stacking [268] techniques, of higher technological complexity.

In this line, we have already shown an improved compositional control and crystalline quality in 12-nm period GaAsSb/GaAsN superlattices [269]. Moreover, the type-II band alignment of GaAsSb/GaAsN superlattices provides additional versatility as compared to bulk GaAsSbN. For instance, the ability to design superlattice structures showing higher carrier radiative lifetimes, which could be expected to allow for an improved carrier collection for both photodetector and photovoltaic applications. However, besides the structural

and compositional impact, the use superlattice structures may bring a major drawback, which is carrier trapping and recombination in the superlattice, before collection. This would result in a lower effective mobility, degrading carrier transport and resulting in a severe reduction of the quantum efficiency [269,270]. Therefore, both radiative lifetime and carrier transport through the superlattice will be ultimately conditioned by its period, which directly affects the electron and hole wavefunction overlap and the electronic coupling between confined states of subsequent periods giving rise to the formation of minibands. In addition, the period thickness will also affect the confinement energies in both the valence and conduction bands, modifying the effective band gap of the superlattice. This appendix is aimed to analyze the tunability of both carrier radiative lifetime and effective band gap through the period thickness in type-II GaAsSb/GaAsN superlattices and its impact on carrier collection. The structural analysis is directly linked to the optoelectronic properties, which is complementary supported by theoretical analyses.

A.2. Sample description

The series of analyzed samples was grown on n^+ -GaAs (001) substrates under As-stabilized conditions. The active region (Fig. A.1 (a)) of a series of samples consist of 200 nm-thick intrinsic GaAsSb/GaAsN superlattices grown at 470 °C and 1 MLs⁻¹. The period thickness was set to 3, 6, 12, and 20 nm (samples SL₃, SL₆, SL₁₂, and SL₂₀, respectively). The expected type-II band structure, with electrons and holes localized in the GaAsN and GaAsSb layers, respectively, and miniband formation are shown in Fig. A.1 (b). The superlattice is embedded between a 250 nm-thick GaAs buffer and a 50 nm-thick cap layer. Equivalent structures to some of these samples have additionally been reproduced in 750 nm-thick layers as the intrinsic region of a p-i-n junction for device fabrication. In these samples buffer and cap layers were n and p-doped, respectively, with nominal concentrations of $2 \cdot 10^{18} \text{ cm}^{-3}$.

Fig. A.1: (a) Sketch of the samples containing 200 nm-thick GaAsSb/GaAsN superlattices and (b) sketch of the expected type-II band structure and miniband formation.

A.3. Results and discussions

A.3.1. Control over lattice-matching condition

The correlation between period thickness, effective band gap and carrier lifetime was investigated in the first series of 200 nm-thick GaAsSb/GaAsN superlattices, which were first structurally analyzed. The alternate introduction of Sb and N in 12 nm-thick period GaAsSb/GaAsN superlattices (SL₁₂) was already found to allow for an accurate control of the Sb and N composition [269], preventing both species from interacting during incorporation to the lattice. Indeed, ternary GaAsSb/GaAs and GaAs/GaAsN superlattices were grown using 3.25% Sb and 1.20% N contents, fulfilling the lattice-matching condition to GaAs, which was satisfied by GaAsSb/GaAsN superlattices grown under the same material source conditions. The Sb and N contents were kept constant while varying the period thickness in SL₃, SL₆, SL₁₂, and SL₂₀. HR-XRD θ -2 θ scans in this series of samples around the GaAs (004) Bragg reflection angle are shown in Fig. A.2. The virtual match of the mean superlattice reflection peak with the substrate Bragg angle in all the samples shows an accurate composition control within the whole range of periodicity in the superlattice structures. Spacing between subsequent satellite peaks allows for a precise estimation of the period thickness, found to be 3.1, 6.3, 12.6, and 19.1 nm for in SL₃, SL₆, SL₁₂, and SL₂₀, respectively, close to the nominal design values.

Fig. A.2: θ - 2θ scans around the (004) Bragg reflection performed on superlattice samples SL₃, SL₆, SL₁₂, and SL₂₀.

A.3.2. Control over effective band gap and carrier lifetime

15 K PL measurements were carried out for a first evaluation of the impact of the superlattice period on the spectroscopic properties. As shown in Fig. A.3, a reduction of the period thickness is found to entail a blueshift of the PL peak. This is expected from the higher confinement energy in thinner QWs, leading to a larger effective band gap. Indeed, the effective band-gap energies in GaAs_{1-x}Sb_x/GaAs_{1-y}N_y superlattices achievable by reducing the period thickness should finally tend to that of a randomly alloyed bulk structure containing the same overall amount of Sb and N, i.e., $x/2$ Sb and $y/2$ N contents [271]. The period thickness of such superlattice structures is therefore an additional parameter, besides the Sb and N contents, allowing for the tunability of the effective bandgap, while keeping lattice-matching condition, in order to reach the wavelengths of interest in a certain field of application. The PL blueshift with the period thickness is accompanied by a FWHM broadening, from ~26 meV in SL₂₀ to 104 meV in SL₃, and enhanced integrated intensity of ~1.6 times from SL₂₀ to SL₃ (inset of Fig. A.3).

Fig. A.3: 15 K PL spectra from the series of superlattice samples SL₃, SL₆, SL₁₂, and SL₂₀. The inset shows the integrated intensity and the FWHM of the PL spectra as a function of the period thickness.

Electronic band structure simulations through finite differences methods help correlate the superlattice period thickness with the optical properties. Fig. A.4 (a) shows the results from calculations taking into account the periods measured by HR-XRD θ -2 θ scans and the expected Sb and N contents in the respective layers. The potential structure and the calculated confined ground states at either conduction and valence band are graphically shown for one GaAsSb/GaN period of SL₃, SL₆, SL₁₂, and SL₂₀. The effective band gap, defined by the ground state transition, is directly tuned by means of the period thickness, decreasing with it. The calculated effective band gap as a function of the period thickness follows a similar tendency as that of the 15 K PL peak energy, shown in Fig. A.4 (b). Indeed, a very good match is found when estimating the 15 K effective band gaps from RT simulations taking into account the particular dependence of band gap energy with temperature in diluted nitrides. Indeed, a lower bandgap shift with temperature is predicted by the BAC model in diluted nitride quantum wells as compared, for example, to GaAs or InGaAs quantum wells [256,272,273]. Simulations additionally reveal an increasing evidence of miniband formation by reducing the period thickness with respect to SL₂₀. Indeed, reducing the period thickness gives rise to broader minibands and a larger density of states, resulting from the stronger interaction among confined states and the higher number of periods. This perfectly correlates with the evolution of the FWHM and the integrated intensity in the PL spectra (inset of Fig. A.3): broader minibands result in broader PL spectra and a larger density of states gives rise to a larger integrated intensity.

Fig. A.4: (a) Electronic band structure simulations through finite differences methods shown for one GaAsSb/GaAsN period of SL₃, SL₆, SL₁₂, and SL₂₀. (b) Effective band gap as a function of the period thickness calculated through finite-differences methods at RT and 15 K, along with the experimental PL peak energy at 15 K.

Time-resolved PL (TR-PL) measurements were carried out at Instituto de Microelectrónica de Madrid (IMM) by B. Alén in order to analyze the tunability of radiative carrier lifetime through the period thickness. Fig. A.5 (a) shows TR-PL decay curves at the PL peak energy from SL₃, SL₆, SL₁₂, and SL₂₀ together with an equivalent bulk GaAsSbN reference sample containing the same nominal amount of Sb and N. The change in the decay dynamics follows a clear tendency whereby thinner period thickness leads to faster PL extinction, the decay behavior progressively approaching that of the bulk material. A multi-exponential fit was carried out in order to describe different regimes in the decay dynamics along the full range of time and quantitatively compare the recombination nature in the different structures. Table 1 shows the characteristic times estimated from the different decay regimes (τ_i), their relative weights (w_i) and the weighted average ($\bar{\tau}$). Decay curves can be well approximated by a double-exponential fit in bulk, SL₃ and SL₆, with characteristic times τ_1 and τ_2 , both with close values in all the samples, showing an increasing average characteristic lifetime with the period thickness. A third decay regime is additionally identified in SL₁₂ and SL₂₀ with longer characteristic time τ_3 and significant relative weight, leading to further increasing average lifetimes. In a first approximation, carrier radiative lifetime can be approximated by the weighted average of the characteristic times in the different decay regimes. This means also assuming that the measured τ_i are the radiative characteristic times, which is a reasonable assumption at low temperature. So estimated radiative lifetimes are represented in Fig. A.5 (b) together with the inverse of the wavefunction overlap, which is directly proportional to the radiative lifetime. Calculations of the wavefunction overlap were carried out by J.M. Llorens (at IMM) using the Nextnano++ package [219]. Simulations were performed

as a function of the period thickness, for both type-I and type-II superlattice structures. The radiative lifetime of the bulk sample and that reported for an equivalent 12 nm-type-I superlattice [269] are additionally represented. There is a good agreement between the tendencies for experimental radiative lifetimes and the theoretically estimated values for the inverse of the wavefunction overlap ($1/\langle\Psi_e|\Psi_h\rangle$). As can be observed, $1/\langle\Psi_e|\Psi_h\rangle$ hardly varies for type-I superlattices and the radiative lifetimes of the 12 nm-type-I superlattice and bulk sample are very close. Therefore, theoretical simulations predict the inability to tune the radiative lifetime of bulk GaAsSbN by means of type-I superlattices. Nevertheless, $1/\langle\Psi_e|\Psi_h\rangle$ increases with the period thickness in type-II superlattices, doing so more significantly above ~ 6 nm period thickness (notice the logarithmical scale). This means low wavefunction overlap characteristic of type-II structures, as expected from the appearance of the third long characteristic radiative lifetime (τ_3) in the decay behavior. On the contrary, the stronger wavefunction overlap, besides the higher density of states, achieved by reducing the period thickness is in agreement with the enhanced integrated intensity of the PL, reducing radiative lifetimes towards near that of the bulk structure (blue dashed line) and of type-I superlattices [269]. This not only means that carrier radiative lifetime can be widely tuned through the period thickness in type-II superlattices, unlike in type-I counterparts, but also that lifetimes characteristic of type-I superlattices are achievable from a type-II one with sufficiently reduced period thickness. Stronger electronic coupling leads therefore to shorter lifetimes. More information on wavefunction overlap or confinement can be obtained from X-STM spectroscopy.

Fig. A.5: (a) 15 K TR-PL decay curves of samples SL₃, SL₆, SL₁₂, SL₂₀, and bulk measured at the PL peak energy. (b) Weighted radiative lifetime of the set of samples and of an equivalent 12 nm-type-I superlattice together with the calculated inverse of the wavefunction overlap as a function of the period thickness in both type-I and type-II superlattice structures. The dotted line indicates the measured carrier lifetime for the bulk sample.

	τ_3 (ns) / w_1 (%)	τ_2 (ns) / w_2 (%)	τ_1 (ns) / w_3 (%)	$\bar{\tau}$ (ns)
SL ₂₀	54.9/55.0	16.2 / 37.0	3.0 / 8.0	36.4
SL ₁₂	49.1 / 24.6	17.0 / 54.7	4.2 / 20.7	22.2
SL ₆	---	16.7 / 84.9	4.1/15.1	14.8
SL ₃	---	15.3 / 82.4	3.0 / 17.6	13.1
bulk	---	15.1 / 76.2	2.9 / 23.8	12.2

Table A.1: Experimental characteristic radiative lifetimes drawn from 15 K TR-PL at the different decay regimes and the weighted lifetime in SL₃, SL₆, SL₁₂, SL₂₀, and bulk samples.

A.3.3. X-STM structural and spectroscopic analysis

X-STM helps go deeper both in the structural and spectroscopic analysis of the set of type-II superlattices. Filled-state topographic scans over areas containing several periods in SL₆ and SL₃ are shown in Fig. A.6 (a) (left) and (b) (left), respectively. These are the samples with thinnest periods, in which interface inhomogeneities and electronic coupling effect may be enhanced to a higher degree. X-STM scans atomically resolve cleaved (110) planes. Large bright and dark features are cleavage-induced defects. Sb and N atoms are commonly seen as brighter and darker dots, respectively, as shown in the inset zoom in Fig. A.6 (a). However, not only Sb and N atoms present in the outer atomic layer are detected by the X-STM probe. Those in several layers underneath may also exert an out-plane relaxation on the surface layer high enough as to be topographically resolved [274], what may hinder an accurate estimation of the average Sb and N contents in the superlattice. Nevertheless, all the Sb- and N-related features can be considered in order to represent the periodicity of the Sb and N profiles throughout the structure.

Fig. A.6 (a) (right) and (b) (right) show the number of Sb and N atoms within each resolved atomic row along the superlattices. The compositional profiles in SL₆ reveals a clear periodicity in both elements in keeping with the periodicity estimated by HR-XRD measurements. Indeed, N-content profile shows an abrupt extinction within the Sb-containing layer with an interface roughness around ± 1 ML. Therefore, the strong Ga-N bonds completely avoid N diffusion and interface variations in the presence of N are most probably due to the step-flow epitaxial growth mechanism. On the contrary, the well-known Sb segregating behavior [275] leads to the presence of a considerable amount of Sb in the N-containing layers, reducing the nominally expected amount of Sb in the GaAsSb layers. As observed in Fig. A.6 (b) (right), the Sb segregation leads to the absence of a clear periodicity in the Sb profile in SL₃. Nevertheless, N still keeps an abrupt content profile even for such small periodicity, with no presence in the GaAsSb layers.

Fig. A.6: X-STM topography image containing several periods of SL_6 (a) (left) and SL_3 (b) (left) along with the Sb and N content profiles along the growth direction (right).

The performance in-situ of cross-sectional tunneling spectroscopy (X-STS) measurements allowed for the analysis of the LDOS at the nanoscale, which is directly proportional to the first derivative of the tunneling current with respect to the applied voltage (see Section 3.3.1). Fig. A.7 shows X-STS measurements along a line crossing several periods of the superlattice structure in SL_{12} (a), SL_6 (b), and SL_3 (c). Despite the clear periodicity observed in the Sb content profile of SL_6 in Fig. A.6 (a), its low impact on the valence band makes it difficult to clearly distinguish a periodicity in the valence-band-related LDOS of any of the superlattices. Nevertheless, the deep electronic states introduced by N induced a clearly observed LDOS periodicity in the conduction band of SL_{12} , while a slight modulation can still be distinguished in SL_6 (notice the different voltage scales). On the contrary, no periodicity

is observed in the LDOS in the conduction band of SL_3 . This result confirms the gradual formation of electronically-coupled minibands by the delocalization of the electronic wavefunction with reducing the period thickness from ~ 12 to ~ 3 nm, in agreement with the reduction of the carrier lifetime. Therefore, strong electronic coupling and miniband formation leads inevitably to short radiative lifetimes. Both electronic coupling and carrier lifetime should have a strong impact on carrier transport through the structure.

Fig. A.7: LDOS measurements along a line crossing several periods of the superlattice structure in SL_{12} (a), SL_6 (b), and SL_3 (c).

A.3.4. Impact of period thickness on carrier transport

To analyze the impact of the superlattice period thickness on carrier transport, the active regions of SL_3 and SL_{12} have been reproduced with a thickness of 750 nm in the intrinsic region of a p-i-n junction (samples SL'_6 and SL'_{12}). Fig. A.8 (a) shows the EQE at RT, directly assessed from PC measurements, of both SL'_6 and SL'_{12} p-i-n devices at 0 V (dashed lines) and at -3 V (continuous lines). -3 V guarantees complete carrier collection, as described in Section 6.3.3 for QDs. The shaded areas represent the energies within the lower and upper miniband energies (red vertical lines) calculated from simulations, which predicted the presence of a single miniband in SL'_6 (1220-1338 meV) and two separated minibands in SL'_{12} (1161-1175 meV and 1276-1358 meV). The respective absorption edges are in good agreement with theoretical calculations for the single miniband edge in SL'_6 and the lower energy miniband edge in SL'_{12} . In addition, the presence of two separated minibands in SL'_{12} is reflected in the presence of a second shoulder in the EQE curve at higher energies closely matching the theoretical predictions. At the other end, there is a large difference in the EQE under short-circuit conditions (0 V) and reverse bias conditions (-3 V) in SL'_{12} , which is no longer present in SL'_6 , showing a small EQE increment at reverse bias. This must be directly related with a more facilitated carrier transport with reduced period thickness, in agreement with the stronger overlap of the electron and hole wavefunctions. Indeed, a significant difference in the wavefunction overlap is found for periods of 6 and 12 nm, falling from around 0.8 in the former case to around 0.2 in the latter one. The evolution of

carrier transport with the applied bias voltage in both structures is directly observed in the I-V measurements shown in Fig. A.8 (b), performed under monochromatic illumination in both SL'_6 and SL'_{12} . Photon energies of 1.20 and 1.28 eV were used respectively, roughly corresponding to the maximum EQE (first miniband in the case of SL'_{12}). While it is necessary to reverse-bias to achieve complete carrier collection in SL'_{12} , it is not so in the case of SL'_6 , in which such a condition is virtually achieved under unbiased conditions [223]. The use of thin period thicknesses, below ~ 6 nm, in type-II GaAsSb/GaAsN superlattices allows therefore an almost complete carrier collection under unbiased conditions, which is of great relevance in both photovoltaic and photodetector devices. Remarkably, this happens despite the increasing radiative lifetimes with reducing the period thickness, so that the facilitated carrier transport overweighs the impact of faster radiative recombination. This means that good carrier transport in type-II superlattices can only be achieved in structures with short carrier lifetimes, a long carrier lifetime being, in principle, incompatible with an adequate transport.

Fig. A.8: (a) EQE at 0 V (dashed lines) and -3 V (continuous lines) of SL'_{12} (left) and SL'_6 (right). Overimposed shaded areas represent the range of energies corresponding to the calculated minibands. (b) I-V curves under monochromatic illumination of SL'_{12} (1.20 eV) and SL'_6 (1.28 eV).

A.4. Conclusions

The spatial separation of both Sb and N, already known to overcome the important epitaxial growth problems the quaternary GaAsSbN faces, has been shown to provide the ability to accurately control the SL period thickness, within a range between ~ 3 and ~ 20 nm, while keeping lattice-matching condition to GaAs. The structural analysis revealed, however, partial segregation of Sb towards the N-containing layers giving rise to a roughly con-

stant Sb content profile for 3 nm superlattice period. Nevertheless, N still keeps the superlattice structure for such thin periods. The tunability of the effective band gap energy and carrier radiative lifetime through the period thickness were both experimentally and theoretically proven. On one side, a reduction of the period thickness leads to larger quantum confinement, increasing the effective band gap. In addition, the stronger interaction between closer contiguous confined states, gives rise to the formation of broader minibands. On the other side, reduced period thicknesses produce shorter radiative lifetimes owing to the stronger wavefunction overlap. Although longer radiative lifetimes are commonly desirable for more efficient carrier collection in both photodetector and photovoltaic devices, the use of shorter period thickness, with enhanced formation of minibands, was found to provide improved carrier transport, despite the faster measured and calculated radiative recombination. Therefore, an efficient carrier collection primarily relies on an efficient carrier transport through electronically coupled minibands achieved for superlattice periods below ~ 6 nm, rather than on the increase of carrier radiative lifetimes. The implementation of such thin-period superlattices in real applications would give rise to weak dark currents, improving the V_{oc} and, therefore, the performance of a solar cell or virtually avoiding thermal noise in photodetection, since no bias would be needed in this case.

B Publications and conferences

B.1. Publications

B.1.1. Book chapters

A.D. Utrilla, D.F. Reyes, J.M. Llorens, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro, and J.M. Ulloa, “*The Impact of Alloyed Capping Layers on the Performance of InAs/GaAs Quantum Dot Solar Cells*”, Advances in Energy Research. Volume 26, Nova Science Publishers, New York (USA), 2017. (ISBN: 978-1-53611-103-3)

B.1.2. Peer-reviewed journal publications

A.D. Utrilla, D.F. Grossi, D.F. Reyes, A. Gonzalo, V. Braza, T. Ben, D. González, A. Guzman, A. Hierro, P.M. Koenraad, and J.M. Ulloa, “*Tuning the metastable state of InAs/GaAs nanostructures through the overgrowth kinetics*”, submitted to Nanoscale.

A. Gonzalo, **A.D. Utrilla**, D.F. Reyes, V. Braza, J.M. Llorens, D.F. Marrón, B. Alén, T. Ben, D. González, A. Guzman, A. Hierro, J.M. Ulloa, “*Strain-balanced type-II superlattices for efficient multi-junction solar cells*”, Sci. Reports. In press.

V. Braza, D.F. Reyes, A. Gonzalo, **A.D. Utrilla**, T. Ben, J.M. Ulloa and D. González, “*Sb and N incorporation interplay in GaAsSbN/GaAs epilayers near lattice matching condition for 1.0-1.16 eV photonic applications*”, Nanoscale Research Letters 12, 356 (2017)

A.D. Utrilla, D.F. Reyes, J.M. Llorens, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Kurtz, A. Guzman, A. Hierro, and J.M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells*”, Solar Energy Materials and Solar Cells 159, 282 (2017).

D.F. Reyes, **A.D. Utrilla**, T. Ben, J.J. Saborido, J.M. Ulloa, G. Bárcena-González, M.P. Guerrero-Lebrero, E. Guerrero, and D. Gonzalez, “*(S)TEM analysis of the strain and morphology of InAs quantum dots using GaAs(Sb)(N) capping layers for solar cell applications*”, Microscopy and Microanalysis 22, Supplement S4, 46 (2016).

G. Bárcena-González, M.P. Guerrero-Lebrero, E. Guerrero, D.F. Reyes, D. González, A. Mayoral, **A.D. Utrilla**, J.M. Ulloa, and P.L. Galindo, “*Strain mapping accuracy improvement using Super-Resolution techniques*”, Journal of Microscopy 262, 50 (2016).

D. González, D.F. Reyes, **A.D. Utrilla**, T. Ben, V. Braza, A. Guzman, A. Hierro, and J.M. Ulloa, “General route for the decomposition of InAs quantum dots during the capping process”, *Nanotechnology* 27, 125703 (2016).

D. Gonzalez, D.F. Reyes, T. Ben, **A.D. Utrilla**, J.M. Ulloa, A. Guzman, and A. Hierro, “Influence of Sb/N contents during the capping process on the morphology of InAs/GaAs quantum dots”, *Solar Energy Materials and Solar Cells* 145, 154 (2016).

A.D. Utrilla, J.M. Ulloa, Ž. Gačević, D.F. Reyes, I. Artacho, T. Ben, D. González, A. Hierro, and A. Guzman, “Impact of alloyed capping layers on the performance of InAs quantum dot solar cells”, *Solar Energy Materials and Solar Cells* 144, 128 (2016).

J.M. Llorens, L. Wewior, E.R. Cardozo de Oliveira, J.M. Ulloa, **A.D. Utrilla**, A. Guzmán, A. Hierro, and B. Alén, “Type-II InAs/GaAsSb quantum dots: Highly tunable exciton geometry and topology”, *Applied Physics Letters* 107, 183101 (2015)

J.M. Ulloa, D.F. Reyes, **A.D. Utrilla**, A. Guzman, A. Hierro, T. Ben, and D. González, “Capping layer growth rate and the optical and structural properties of GaAsSbN-capped InAs/GaAs quantum dots”, *Journal of Applied Physics* 116, 134301 (2014).

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A.D. Utrilla, J.M. Ulloa, A. Guzman, and A. Hierro, “Long-wavelength room-temperature luminescence from InAs/GaAs quantum dots with an optimized GaAsSbN capping layer”, *Nanoscale Research Letters* 9, 36 (2014).

A. D. Utrilla, J. M. Ulloa, A. Guzmán, and A. Hierro, “Impact of the Sb content on the performance of GaAsSb-capped InAs/GaAs quantum dot lasers”, *Applied Physics Letters* 103, 111114 (2013).

B.1.3. Peer-reviewed proceeding publications

A.D. Utrilla, D.F. Reyes, J.M. Llorens, A. Gonzalo, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro, and J. M. Ulloa, “Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells”, *Proceedings of the 32nd European Photovoltaic Solar Energy Conference and Exhibition*, 32 (2016). (ISBN: 3-936338-41-8)

A.D. Utrilla, J.M. Ulloa, Ž. Gačević, D.F. Reyes, D. González, T. Ben, Á. Guzmán, and A. Hierro, “*Stacked GaAs (Sb)(N)-capped InAs/GaAs quantum dots for enhanced solar cell efficiency*”, Proceedings of the Optoelectronics and Photonic Materials and Devices Conference SPIE OPTO 9358, 93580J (2015). (ISBN: 9781628414486)

B.1.4. Other publications

D. F. Reyes, V. Braza, A. Gonzalo, **A.D. Utrilla**, D.F. Grossi, P.M. Koenraad, A. Guzman, A. Hierro, J. M. Ulloa, T. Ben, and D. González, “*Analysis of the Sb and N distribution in GaAsSb/GaAsN superlattices for solar cell applications*”, European Microscopy Congress 2016: Proceedings, 570-571. (2016). (ISBN: 9783527808465).

D.F. Reyes, V. Braza, **A.D. Utrilla**, T. Ben, A. Guzman, A. Hierro, J.M. Ulloa, and D. González. “*Analysis of capping with GaAsSbN thin layers in (un)coupled InAs/GaAs multi quantum dot layers for enhanced solar cells*”, European Microscopy Congress 2016: Proceedings, 912–913 (2016). (ISBN: 9783527808465).

B.2. Conference contributions

B.2.1. Invited oral presentations

J.M. Ulloa, A. Gonzalo, **A.D. Utrilla**, D.F. Reyes, V. Braza, J.M. Llorens, D. Fuertes Marrón, B. Alén, T. Ben, D. González, A. Guzman and A. Hierro, “*Strain-balanced type-II superlattices for efficient multi-junction solar cells*”, Bit’s Annual World Congress of Advanced Materials. Xi’an (China), June 14-16, 2017.

J.M. Ulloa, **A.D. Utrilla**, D.F. Reyes, A. Gonzalo, T. Ben, Ž. Gačević, D. González, A. Guzman and A. Hierro, “*Modified InAs/GaAs quantum dots for enhanced solar cell efficiency*”, Energy Materials and Nanotechnology Collaborative Conference on Crystal Growth. Hong Kong (China), December 14-17, 2015.

J.M. Ulloa, **A.D. Utrilla**, A. Guzman, A. Hierro, D.F. Reyes, D. Gonzalez, J. Keizer and P.M. Koenraad, “*GaAs(Sb)(N)-capped InAs/GaAs quantum dots: from atomic scale characterization to improved device performance*”, Energy Materials and Nanotechnology Fall Meeting. Orlando (USA), December 7-10, 2013.

B.2.2. Oral presentations

V. Braza, A. Gonzalo, D.F. Reyes, **A.D. Utrilla**, J.M. Ulloa, T. Ben, J.M. Llorens, B. Alén, and D. González, “*New growth approaches to improve the performance in GaAsN-based solar cells*”, 9th International Conference on Advance Nano Materials. Aveiro (Portugal). July 19-21, 2017.

D.F. Reyes, V. Braza, **A.D. Utrilla**, A. Gonzalo, J.M. Ulloa, T. Ben, and D. González, “*Effect of the capping layer composition and growth rate in the InAs quantum dots/wetting layer system*”, Microscience Microscopy Congress 2017. Manchester (United Kingdom). July 3-6, 2017.

A. Gonzalo, **A.D. Utrilla**, A. Arruebo, D.F. Reyes, V. Braza, J.M. Llorens, D.F. Marrón, B. Alén, T. Ben, D. González, A. Guzmán, A. Hierro, and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices for efficient multi-junction solar cells*”, 41st Workshop on Compound Semiconductor Devices and Integrated Circuits held in Europe. Las Palmas de Gran Canarias (Spain). May 21-24, 2017.

A.D. Utrilla, A. Gonzalo, D.F. Grossi, D.F. Reyes, V. Braza-Blanco, B. Alén, D.F. Marrón, P.M. Koenraad, T. Ben, D. González, A. Guzmán, A. Hierro, and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices as 1 eV layer for efficient multi-junction solar cells*”, 19th International Conference on Molecular Beam Epitaxy. Montpellier (France), September 4-9, 2016.

D.F. Reyes, V. Braza, A. Gonzalo, **A.D. Utrilla**, D.F. Grossi, P.M. Koenraad, A. Guzman, A. Hierro, J.M. Ulloa, T. Ben, and D. González, “*Analysis of the Sb and N distribution in GaAsSb/GaAsN superlattices for solar cell applications*”, The 16th European Microscopy Congress. Lyon (France), August 28 - September 2, 2016.

A.D. Utrilla, D.F. Reyes, J.M. Llorens, A. Gonzalo, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro, and J.M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells*”, European Photovoltaic Solar Energy Conference and Exhibition 2016, Munich (Germany), June 20-24, 2016.

V. Braza, D.F. Reyes, A. Gonzalo, **A.D. Utrilla**, J.M. Ulloa, A. Hierro, A. Guzman, T. Ben, and D. González, “*Análisis de la interdifusión en superredes de GaNAsSb para aplicaciones en celdas solares de multiunión*”, XIV Congreso Nacional de Materiales. Gijón (Spain), June 8-10, 2016.

G. Bárcena-González, M.P. Guerrero-Lebrero, E. Guerrero, D.F. Reyes, D. González, A. Mayoral, **A.D. Utrilla**, J.M. Ulloa, and P.L. Galindo, “*Quality enhancement and strain*

measurement in HAADF images using Super-Resolution techniques”, 11th Asia-Pacific Microscopy Conference, Phuket (Thailand), May 23-27, 2016.

V. Braza-Blanco, D.F. Reyes, T. Ben, **A.D. Utrilla**, J.M. Ulloa, and D. González, “General decomposition route of InAs quantum dots during the capping process”, 2015 European Materials Research Society Fall Meeting. Warsaw (Poland), September 15-18, 2015.

D.F. Reyes, **A.D. Utrilla**, T. Ben, J. J. Saborido, J.M. Ulloa, G. Bárcena-González, and D. Gonzalez. “(S)TEM Analysis of the Strain and Morphology of InAs Quantum Dots using GaAs(Sb)(N) capping layers for Solar Cell Applications”, Microscopy at the frontiers of science 2015. Porto (Portugal), September 9-11, 2015.

T. Ben, D. Gonzalez, D.F. Reyes, **A.D. Utrilla**, J.M. Ulloa, A. Guzman, and A. Hierro, “Influence of Sb/N contents during the capping process on the morphology of InAs/GaAs quantum dots”, 2015 European Materials Research Society Spring Meeting. Lille (France), May 11-15, 2015.

A.D. Utrilla, J. M. Ulloa, Ž. Gačević, D.F. Reyes, D. González, T. Ben, A. Guzman and A. Hierro, “Stacked GaAs(Sb)(N)-capped InAs/GaAs quantum dots for enhanced solar cell efficiency”, SPIE Photonics West 2015. San Francisco (USA), February 7-12, 2015.

A.D. Utrilla, J.M. Ulloa, Ž. Gačević, A. Guzman, and A. Hierro, “Stacked GaAs(Sb)(N)-capped InAs/GaAs quantum dots for enhanced solar cell efficiency”, Nanostructures for Solar Cells. Braga (Portugal), October 2-3, 2014.

A.D. Utrilla, J.M. Ulloa, Ž. Gačević, A. Guzman, and A. Hierro, “Stacked GaAs(Sb)(N)-capped InAs/GaAs quantum dots for enhanced solar cell efficiency”, 18th International Conference on Molecular Beam Epitaxy. Flagstaff (USA), September 7-12, 2014.

A.D. Utrilla, J. M. Ulloa, L. Domínguez, D. F. Reyes, D. González, A. Guzman, and A. Hierro, “Room temperature luminescence beyond 1.3 μm from GaAsSbN-capped InAs quantum dots”, Novel Gain Materials and Devices Based on III-V-N/Bi Compounds. Istanbul (Turkey), September 24-26, 2013.

B.2.3. Poster presentations

V. Braza, D. F. Reyes, **A. D. Utrilla**, A. Gonzalo, T. Ben, J. M. Ulloa, and D. González, “Evolution of InAs quantum dots/wetting layer system under different GaAs capping layer growth rates”, 20th Microscopy of Semi Conducting Materials. Oxford (United Kingdom). April 9 - 13, 2017.

A. Gonzalo, **A. D. Utrilla**, D. F. Reyes, V. Braza-Blanco, B. Alén, D. F. Marrón, T. Ben, D. González, A. Guzmán, A. Hierro, and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices for efficient multi-junction solar cells*”, 32nd North American Conference on Molecular Beam Epitaxy. New York (USA), September 18 - 21, 2016.

D.F. Reyes, V. Braza, **A.D. Utrilla**, T. Ben, A. Guzman, A. Hierro, J.M. Ulloa, and D. González, “*Analysis of capping with GaAsSbN thin layers in (un)coupled InAs/GaAs multi quantum dot layers for enhanced solar cells*”, The 16th European Microscopy Congress. Lyon (France), August 28 - September 2, 2016.

G. Bárcena-González, M.P. Guerrero-Lebrero, E. Guerrero, D.F. Reyes, D. González, A. Mayoral, **A.D. Utrilla**, J.M. Ulloa, and P.L. Galindo, “*Strain measurement inside dumbbells in HAADF images using Super-Resolution techniques*”, The 16th European Microscopy Congress. Lyon (France), August 28 - September 2, 2016.

A.D. Utrilla, A. Gonzalo, J.M. Llorens, A. Guzman, A. Hierro, and J.M. Ulloa, “*Role of the wetting layer in the performance of quantum dot solar cells*”, 2016 European Materials Research Society Spring Meeting. Lille (France), May 2-6, 2016.

A. Gonzalo, **A.D. Utrilla**, D.F. Reyes, V. Braza-Blanco, D. Fuertes Marrón, T. Ben, D. González, A. Guzman, A. Hierro, and J.M. Ulloa, “*Strain-balanced GaAsSb-GaAsN type-II superlattices as 1eV layer for efficient multi-junction solar cells*”, 2016 European Materials Research Society Spring Meeting. Lille (France), May 2-6, 2016.

E.R. Cardozo, M.D. Teodoro, V. Lopez-Richard, G.E. Marques, J. Llorens, L. Wewior, B. Alén, J.M. Ulloa, **A.D. Utrilla**, A. Guzmán, and A. Hierro, “*Modulation of Confinement Topology on InAs/GaAsSb quantum dots induced by electric field*”, XIV Brazil Materials Research Society Meeting. Rio de Janeiro (Brazil), September 27 - October 1, 2015.

A.D. Utrilla, J.M. Ulloa, Ž. Gačević, D. F. Reyes, D. González, T. Ben, Á. Guzmán, and A. Hierro, “*GaAs(Sb)(N)-capped InAs/GaAs quantum dots for enhanced solar cell efficiency*”, 18th European Molecular Beam Epitaxy Workshop. Canazei (Italy), March 15-18, 2015.

J. M. Ulloa, **A.D. Utrilla**, Ž. Gačević, D. F. Reyes, D. González, T. Ben, A. Guzman, and A. Hierro, “*Type-I and type-II InAs/GaAs Quantum dot solar cells with a GaAsSb capping layer*”, 18th European Molecular Beam Epitaxy Workshop. Canazei (Italy), March 15-18, 2015.

J. M. Ulloa, D.F. Reyes, **A. D. Utrilla**, A. Guzman, A. Hierro, T. Ben, and D. González, “*Capping layer growth rate and the optical and structural properties of GaAsSbN-capped InAs/GaAs quantum dots*”, SPIE Photonics West 2015. San Francisco (USA), February 7-12, 2015.

A.D. Utrilla, J.M. Ulloa, A. Guzman, and A. Hierro, “*Impact of a thin GaAsSb capping layer on the lasing characteristics of InAs/GaAs quantum dot lasers*”, 17th European Molecular Beam Epitaxy Workshop. Levi (Finland), March 10-13, 2013.

B.2.4. Awards and merits

- Winner of the 20th Microscopy of Semi Conducting Materials conference 2nd Poster Prize in the symposium of “Strained Layers and Quantum Wells”.

V. Braza, D. F. Reyes, **A. D. Utrilla**, A. Gonzalo, T. Ben, J. M. Ulloa, and D. González, “*Evolution of InAs quantum dots/wetting layer system under different GaAs capping layer growth rates*”, 20th Microscopy of Semi Conducting Materials. Oxford (United Kingdom). April 9-13, 2017.

- Winner of the 2016 European Photovoltaic Solar Energy Conference and Exhibition Student Award for “the most outstanding student research work in the field of New Materials and Concepts for Cells”.

A. D. Utrilla, D. F. Reyes, J. M. Llorens, A. Gonzalo, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro, and J. M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells*”, European Photovoltaic Solar Energy Conference and Exhibition 2016, Munich (Germany), June 20-24, 2016.

- Winner of the 2016 European Materials Research Society Spring Meeting best poster award in the symposium of “Advanced materials and characterization techniques for solar cells III”.

A. Gonzalo, **A.D. Utrilla**, D.F. Reyes, V. Braza-Blanco, D. Fuertes Marrón, T. Ben, D. González, A. Guzman, A. Hierro, and J.M. Ulloa, “*Strain-balanced GaAsSb-GaAsN type-II superlattices as 1eV layer for efficient multi-junction solar cells*”, 2016 European Materials Research Society Spring Meeting. Lille (France), May 2-6, 2016.

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